W. Theilheimer

Synthetic Methods of Organic Chemistry

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W. Theilheimer

Synthetic Methods of Organic Chemistry

An Annual Survey

Synthetische Methoden der Organischen Chemie

Jahrbuch

Vol. 10

With Reaction Titles and Cumulative Index of Volumes 6–10

Mit Titeln und Generalregister der Bände 6–10

Mit deutschem Register-Schlüssel

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BASEL (Switzerland) S. KARGER NEW YORK

For the Western Hemisphere: Interscience Publishers, Inc., New York
For Great Britain: Interscience Publishers, Ltd., London

English Translations			*Deutsche Ausgaben*
1948 Interscience Publishers	*Vol. I*	1946	1. Auflage
		1948	2. unveränderte Auflage
		1950	3. unveränderte Auflage
1949 Interscience Publishers	*Vol. II*	1948	
	Vol. III	1949	with English Index Key
		1953	2. unveränderte Auflage
	Vol. IV	1950	with English Index Key

English Editions *Mit deutschem Register-Schlüssel*			
	Vol. V	1951	With Reaction Titles Vol. I–V and Cumulative Index
	Vol. VI	1952	
	Vol. VII	1953	
	Vol. VIII	1954	
	Vol. IX	1955	

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Printed in Switzerland by Friedrich Reinhardt AG., Basel

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From the Prefaces to the Preceding Volumes

New methods for the synthesis of organic compounds, improvements of known methods, and also old proved methods scattered in periodicals, are being recorded continuously in this book series.

An attempt has been made to develop the system of Weygand (Organic Preparations, Interscience Publishers, Inc., New York, 1945), and to group the reactions on a simple, although purely formal, basis. This has led to the invention of reaction symbols that can be classified systematically so that the methods can be treated without knowledge of the current trivial and author names (e.g., "Oxidation" and "Friedel-Crafts reaction").

Readers accustomed to the common notations will find these in the subject index. In many cases, particularly in searching for complex reactions, use of the classification system may be avoided by consulting the subject index. It is thought that the volumes should be kept close at hand. They should provide a quick survey, and obviate the immediate need for an elaborate library search. Syntheses are therefore recorded in the subject index by starting materials and end products, along with the systematic arrangement for the methods. This makes possible a sub-classification within the reaction symbols by reagents, a further methodical criterion. Complex compounds are indexed with cross references under the related simpler compounds. General terms, such as synthesis, replacement, heterocyclics, may also be brought to the special attention of the reader.

Starting with Volume 5, a table that indicates the sequence of the reagents has been included. It may help the reader to locate reactions in the body of the text, particularly within large chapters. This table also contains such frequently used reagents as NaOH and HCl, which are not included in the alphabetical index.

Volume 8 and subsequent volumes contain a brief review, Trends in Synthetic Organic Chemistry, stressing some highlights of general interest and calling attention to developments too recent to be included in the body of the text.

The abstracts are limited to the information needed for an appraisal of the applicability of a desired synthesis. This includes the number and nature of the reaction steps, the yield, and the important literature in question. In order to carry out a particular synthesis it is therefore still necessary to have recourse to the original papers or, at least, to an abstract journal. In order to avoid repetition, selections are made on the basis of most detailed description and best yields, whenever the same method is used in similar cases. Continuations of papers already included will not be abstracted, unless they contain essentially new information. They may, however, be quoted at the place corresponding to the abstracted papers. These supplementary references make it possible to keep abstracts of previous volumes up-to-date.

Furthermore, to avoid a "jungle" of references, the following limitations have been decided on: Papers are not included, if their content does not fit the subject matter of "Synthetic Methods" and if they can be found easily in the indexes of the abstract journals. Less accessible and readable papers, such as the Russian or Japanese ones, are only abstracted, as a rule, if the method in question is described nowhere else. Since publications dealing with organic chemistry are increasing from year to year, some unintentional omissions may occur as well. Therefore, the editor will be grateful if important methods not yet mentioned are brought to his attention.

Syntheses that are split into their various steps, which are recorded in different places, can be followed with the help of the notations *startg. m. f.* (starting material for the preparation of ...) and *prepn. s.* (preparation, see).

Aus den Vorworten zu den vorhergehenden Bänden

In dieser Buchreihe sollen neue Methoden zur Synthese organischer Verbindungen, Verbesserungen bekannter und auch bewährte ältere Methoden, die sich in den in Fachzeitschriften veröffentlichten Originalarbeiten verstreut vorfinden, laufend registriert werden.

Aufbauend auf der Weygandschen Systematik wurde versucht, alle Reaktionen an Hand weniger einfacher, wenn auch rein formaler Richtlinien zu ordnen. Dies führte zur Ausarbeitung von Reaktions-Formelzeichen, die sich im Gegensatz zu den bisherigen Trivial- bzw. Autorennamen, wie Oxydation, Friedel-Crafts-Synthese, systematisch anordnen lassen. Man kann so die Methoden, ohne ihren Namen zu kennen, mittels des Formelzeichens auffinden.

Benutzer, die an die alten Bezeichnungen gewöhnt sind, finden diese im alphabetischen Register, das in vielen Fällen den Gebrauch der Systematik entbehrlich machen und besonders zum Aufsuchen komplizierter Reaktionen mit Vorteil benutzt werden dürfte. Da die Sammlung für die Handbibliothek am Arbeitsplatz im Laboratorium gedacht ist, soll sie eine rasche Orientierung gestatten, ohne daß fürs erste die Literatur der Instituts- oder Werkbibliothek herangezogen werden muß. Neben der systematischen Registrierung der Methoden werden deshalb im alphabetischen Register auch Synthesen durch ihre Ausgangs- und Endprodukte registriert. Dies ermöglicht es, im Text, innerhalb der Reaktionszeichen, nach einem weiteren methodischen Kriterium, nämlich den Hilfsstoffen einzuteilen. Neuartig ist ferner die Registrierung der komplizierten Verbindungen. Auf Sammelbegriffe wie Aufbau, Austausch, Heterocyclen sei noch besonders hingewiesen.

Beginnend mit Band 5 ist eine Tafel aufgenommen worden, die die Reihenfolge der Hilfsstoffe angibt. Sie dürfte zum Aufsuchen von Reaktionen im Text, besonders in großen Kapiteln, nützlich sein. Sie enthält auch so häufig gebrauchte Hilfsstoffe wie NaOH und HCl, die im alphabetischen Register nicht aufgeführt sind.

Band 8 und die folgenden Bände enthalten einen kurzen Überblick, «Trends in Synthetic Organic Chemistry», der einige der wichtigsten Fortschritte allgemeinen Interesses aufzeigt und auf neue Arbeiten hinweist, die nicht mehr in den Hauptteil des Bandes aufgenommen werden konnten.

Die Referate beschränken sich auf das zur Beurteilung der Zweckmäßigkeit einer Synthese Notwendige, wie Zahl und Art der Reaktionsstufen, die Ausbeute, wichtige, die Methode betreffende Literatur usw. Vor Ausführung einer bestimmten Synthese ist es deshalb erforderlich, das chemische Zentralblatt oder ein anderes Referatenblatt und, wenn möglich, auch die Originalarbeit zu Rate zu ziehen. Zur Vermeidung von Wiederholungen wurden bei der Anwendung einer Methode in ähnlichen Fällen diejenigen ausgewählt, die am ausführlichsten beschrieben sind und die besten Ausbeuten geben. Fortsetzungen bereits aufgenommener Arbeiten, die nichts wesentlich Neues bringen, werden nicht mehr referiert, evtl. aber an der Stelle der aufgenommenen Arbeit zitiert. Diese Ergänzungszitate ermöglichen es, Referate aus früheren Bänden auf den neuesten Stand zu bringen.

Um ferner das Material nicht zu sehr auf Kosten der Uebersicht anschwellen zu lassen, werden Veröffentlichungen, die nicht ganz in den Rahmen der «Synth. Meth.» passen und die in den Sachregistern der Referatenblätter leicht aufgefunden werden können, nicht aufgenommen. Arbeiten aus schwerer zugänglichen und lesbaren Zeitschriften, wie z. B. den russischen und japanischen, werden im allgemeinen nur dann referiert, wenn die betreffende Methode sonst nirgends beschrieben ist. Da die Zahl der Veröffentlichungen auf dem Gebiete der organischen Chemie von Jahr zu Jahr zunimmt, unterbleibt die Aufnahme von Arbeiten manchmal auch unabsichtlich. Wir wären deshalb dankbar, wenn wir auf wichtige Methoden aufmerksam gemacht würden, die in unserer Sammlung noch nicht enthalten sind.

Synthesen, die in ihre Stufen zerlegt und an verschiedenen Stellen eingeordnet sind, können mit Hilfe der Vermerke *startg. m. f.* (Ausgangsmaterial für die Darstellung von . . . und *prepn. s.* (Darstellung siehe) zusammengesetzt werden.

Preface to Volume 10

Most of the entries in this volume are abstracts of papers published between 1953 and 1955. This is the final volume of the second series; it contains a cumulative alphabetical index for Volumes 6 to 10 and, in the body of the text, all reaction titles of these volumes. This arrangement reduces a five-volume search to a search through a single volume. As in Volume 5, the costly preparation of a separate index volume has again been avoided by combining the publication of a cumulative index with that of new material.

I want to thank Dr. John T. Plati once more for having checked the manuscript and Dr. Bernhard Prijs for his thorough proof-reading. I also greatly appreciate the valuable advice they have given me. Thanks are due again to Dr. J. A. Aeschlimann, Vice President of Hoffmann-La Roche, Inc., for liberally providing me with library and office facilities.

Nutley, New Jersey, U.S.A., May 1956.

W. Th.

Vorwort zu Band 10

Der vorliegende Band 10 der «Synthetischen Methoden» bringt hauptsächlich Referate von Arbeiten aus den Jahren 1953—1955. Als letzter Band der zweiten Serie enthält er ein Generalregister für die Bände 6—10 und, im Text, alle Titel dieser Bände. Diese Anordnung reduziert ein fünfmaliges Aufsuchen einer Methode auf ein einmaliges Nachschlagen. Dadurch, daß wieder ein Generalregister mit einer Sammlung neuer Referate vereinigt wurde, konnten die Kosten für einen separaten Registerband vermieden werden.

Nutley, New Jersey, USA., im Mai 1956.

W. Th.

Method of Classification

The following directions serve to explain the system of Classification.

1. Reaction Symbols.

The first part of the symbol refers to the chemical bonds formed during the reaction. These bonds appear in the reaction symbols as the symbols for the two elements that have been linked together (e.g., the bond between hydrogen and nitrogen, as HN). The order of the elements is the same as in *Chemisches Zentralblatt* and in Beilstein's *Handbuch der organischen Chemie:* H, O, N, Hal (Halogen), S, and the remaining elements (Rem). C is always placed last.

The "principle of the latest position" determines the order of the element symbols, and is used whenever possible.

The methods of obtaining a particular chemical bond are subdivided according to methods of formation. Four types are distinguished: addition (⇓), rearrangement (⤵), exchange (⇅), and elimination (⇑). The last part of the symbol refers to the bonds which are destroyed in the reaction or to a characteristic element of that part of the molecule which is eliminated.

The following simplifying stipulations facilitate the use of the reaction symbols: *(1)* The chemical bond is rigidly classified according to the structure formula without taking the reaction mechanism into consideration. *(2)* Double or triple bonds are treated as being equivalent to two or three single bonds, respectively. *(3)* Generally speaking, only stable organic compounds are taken into consideration. Intermediary compounds, such as Grignard compounds and sodiomalonic esters, and anorganic reactants, such as nitric acid, are therefore not expressed in the reaction symbols.

Examples:
see Volume II, page viii

Systematic Survey
see page 727

2. Reagents.

A further subdivision, not included in the reaction symbols, is made on the basis of the reagents characteristic of the reaction. The order usually follows that of the periodic system. Reagents made up of several components are arranged according to the element significant for the reaction (e.g., $KMnO_4$ under Mn, NaClO under Cl). When a constituent of the reagent goes into the products of the reaction, the remainder of the reagent, which acts as a carrier of this constituent, is the criterion for the classification; for example, phosphorus is the carrier in a chlorination with PCl_5 and sodium in a nitrosation with $NaNO_2$. A table indicating the sequence of the reagents may be found on page 730.

3. The material between the listings of the reagents is arranged with the simple examples first and the more complicated ones following.

4. When changes in more than one chemical bond occur during a reaction, as, for example, in the formation of a new ring, or if the reaction can be carried out in different ways, these reactions are introduced in several places when necessary. The main entry in such cases is placed usually according to the "principle of the latest position"; the other entries are cross-referenced back to it.

Systematik

Für die Reihenfolge der Methoden gelten folgende Richtlinien:

1. Reaktionszeichen.

Die Einteilung erfolgt zuerst nach den Bindungen, die bei einer Reaktion entstehen. Diese erscheinen im Reaktions-Formelzeichen in Gestalt ihrer beiden Elementsymbole, z. B. die Bindung zwischen Wasserstoff und Stickstoff als HN. Die Reihenfolge der Elemente ist die gleiche wie im Chemischen Zentralblatt und in Beilsteins Handbuch der organischen Chemie: H, O, N, Hal (Halogen), S, Rem (Uebrige Elemente), C steht an letzter Stelle.

Das «*Prinzip der letzten Stelle*» bestimmt die Reihenfolge der Elementsymbole und ist auch sonst nach Möglichkeit immer angewandt worden.

Die Methoden zur Herstellung einer bestimmten Bindung werden nach ihrer Bildungsweise eingeteilt. Es werden 4 Fälle unterschieden: Aufnahme (⇓), Umlagerung (↷), Austausch (⇵) und Abgabe (⇑).

Der letzte Teil des Reaktionszeichens gibt die Bindung an, die gelöst wird, oder ein charakteristisches Element desjenigen Molekülteils, der abgespalten wird.

Die Bildung des Reaktionszeichens wird durch folgende vereinfachende Annahmen erleichtert:

1. Die Bindungen für die Registrierung ergeben sich rein formal aus den Strukturformeln, ohne daß auf Reaktionsmechanismen Rücksicht genommen wird.
2. Doppel- und Dreifachbindungen werden 2 bzw. 3 Einfachbindungen gleichgesetzt.
3. Es werden in der Regel nur stabile organische Verbindungen berücksichtigt, Zwischenprodukte, wie z. B. Grignard-Verbindungen, Na-Malonester und anorganische Reaktionspartner, wie z. B. Salpetersäure, werden deshalb nicht zur Bildung des Reaktionszeichens herangezogen.

Beispiele

siehe Band 2, Seite VI.

Systematische Uebersicht

siehe Seite 727.

2. Hilfsstoffe.

Eine weitere Unterteilung, die im Reaktionszeichen nicht mehr zum Ausdruck kommt, wird nach den für die Reaktion charakteristischen Hilfsstoffen vorgenommen. Ihre Reihenfolge richtet sich im wesentlichen nach dem periodischen System. Hilfsstoffe, die sich aus mehreren Bestandteilen zusammensetzen, werden nach demjenigen eingeteilt, der für die Reaktion verantwortlich ist. z. B. steht $KMnO_4$ bei Mn, NaClO bei Cl. Geht ein Bestandteil des Hilfsstoffs in das Reaktionsprodukt ein, dann ist der Rest als Träger dieses Bestandteils für die Einordnung maßgebend; das ist z. B. bei einer Chlorierung mit PCl_5 Phosphor, bei einer Nitrosierung mit $NaNO_2$ Natrium. Eine Tafel der Reihenfolge der Hilfsstoffe befindet sich auf Seite 730.

3. Innerhalb dieser Unterteilung sind die einzelnen Referate von einfachen zu komplizierten Beispielen fortschreitend angeordnet.

4. Treten bei einer Reaktion Veränderungen an mehreren Bindungen ein, wie z. B. bei Ringschlüssen, oder kann sie auf verschiedene Art durchgeführt werden, dann wird sie, falls notwendig an mehreren Stellen eingeordnet. Das Hauptzitat steht in diesen Fällen in der Regel an der letzten Stelle; an den übrigen Stellen befinden sich Hinweise auf dieses.

Trends

in Synthetic Organic Chemistry

1956

Intensive work continues on the —CONH— linkage, which plays such a basic role in nature. Various methods for the easy formation of this linkage are being investigated, such as the use of activated esters[1], or of alkoxyacetylene as a reagent[2]. Brenner[3] has shown the unique potentialities of salicylic acid in peptide chemistry. The following reactions have been applied in this field: Esterification with thionyl chloride (*9*, 344), recently used in a simplified oxytocin synthesis[4], and esterification with polyphosphoric acid[5]. N-Trifluoroacetyl derivatives[6] have been made with ethyl thioltrifluoroacetate (*10*, 374). Mixed alkoxyformic anhydrides, originally applied in peptide chemistry, are currently finding their way into other fields of organic synthesis and have recently been used in C-acylations[7].

An interesting indole ring synthesis[8] and a recent synthesis of benzofuran derivatives[9] are results of the extensive work done by Adams and coll. on quinone imides. Kröhnke and coll., while exploring the potentialities of pyridinium and related salts as intermediates have added syntheses of isatogens (*8*, 564; *9*, 733), of desoxybenzoins[10], and of certain 2-aminoalcohols[11] to their well-known aldehyde synthesis. Nitrilium salts are the subject of investigations by Meerwein and coll., who used them for a new quinazoline synthesis[12]. Ziegler's well-known work on organoaluminum compounds has yielded an interesting synthesis of prim. alcohols from methylene compounds[13]. This reaction proceeds contrary to the direction indicated by Markownikoff's rule. Recently, pure *cis*-olefins have been prepared from acetylene derivatives by means of dialkylaluminum hydrides[14]. By the way, the Lindlar catalyst is now widely used in the semi-hydrogenation of triple bonds[15].

---

[1] Synth. Meth. *10,* 299; Helv. *39,* 57 (1956).

[2] J. F. Arens, R. *74,* 769 (1955).

[3] M. Brenner et al., Experientia *11,* 397 (1955).

[4] R. A. Boissonnas et al., Helv. *38,* 1491 (1955).

[5] B. F. Erlanger and R. M. Hall, Am. Soc. *76,* 5781 (1954); J. D. Cipera and R. V. V. Nicholls, Chem. and Ind. *1955,* 16.

[6] cf. F. Weygand and R. Geiger, B. *89,* 647 (1956).

[7] D. S. Tarbell and J. R. Price, J. Org. Chem. *21,* 144 (1956).

[8] R. Adams and W. P. Samuels, Am. Soc. *77,* 5375, 5383 (1955).

[9] R. Adams and L. Whitaker, Am. Soc. *78,* 658 (1956).

[10] F. Kröhnke and I. Vogt, A. *589,* 26 (1954).

[11] F. Kröhnke and I. Vogt, A. *589,* 45 (1954).

[12] H. Meerwein et al., B. *89,* 224 (1956).

[13] K. Ziegler et al., A. *589,* 91 (1954); Ang. Chem. *67,* 425 (1955).

The most remarkable new single reaction is the Wittig synthesis of ethylene derivatives from oxo compounds. The carbon-carbon double bond takes the place of the carbon-oxygen double bond, whereas the isomers usually result by the Saytzeff elimination involved in other methods. This synthesis has already been used by several laboratories[16]. Other items concerning unsaturation are the following: A new method of dehalogenation by the use of NaH and alcohol[17] and a new dehydrocyanation reaction[18]. Work on an industrial carotenoid synthesis has been published by Isler and coll.[19], in which the acetal-enolether condensation (cf. *7*, 724) is repeatedly used to lengthen the chain of unsatd. aldehydes. The same team used a modified Whiting reaction to transform acetylenediols into dienes[20].

As concerns oxo compounds, a synthesis of aldehydes deserves mentioning, which is suitable for the preparation of compounds labeled at the aldehyde C-atom[21]. The aldehyde synthesis with formamides, especially dimethylformamide, is discussed in new publications (*10*, p. 494). There is also a paper on the protection of aldehyde groups by the formation of 1,1-diacetates (*10*, 135) and a recent account of a convenient method for reducing acid chlorides to aldehydes by using lithium tri-*tert*-butoxyaluminum hydride[22]. Other papers describe an easy cleavage of dinitrophenylhydrazones (*10*, 179), the preparation of ketols from enacetamides as applied to steroids (*10*, 175), of α-diketones from α-nitratoketones[23], and, finally, of ω-halogenoketones by the rearrangement of *tert.* cycloaliphatic hypohalites[24].

The preparation of esters and other acid derivatives with arylsulfonyl chlorides in pyridine has been recommended[25]. Esters which are sterically hindered can be prepared with trifluoroacetic anhydride as a catalyst (*6*, 211; *10*, p. 153). Nitriles can be made from amides under mild conditions (*10*, 292), and BF_3 has been recommended for the reverse reaction[26].

---

[14] G. Wilke and H. Müller, B. *89*, 444 (1956).

[15] Synth. Meth. *7*, 95; *10*, p. 64; Helv. *39*, 249 (1956).

[16] Synth. Meth. *10*, 633; I. T. Harrison, B. Lythgoe, and S. Tripett, Soc. *1955*, 4016; H. H. Inhoffen, K. Brückner, and H.-J. Hess, B. *88*, 1850 (1955); O. Isler et al., Helv. *39*, 463 (1956).

[17] M. S. Newman and S. H. Merrill, Am. Soc. *77*, 5549 (1955).

[18] C. R. Hauser and W. R. Brasen, Am. Soc. *78*, 82 (1956).

[19] O. Isler et al., Helv. *39*, 249, 259, 463 (1956).

[20] O. Isler et al., Helv. *39*, 454 (1956).

[21] H. M. Fales, Am. Soc. *77*, 5118 (1955).

[22] H. C. Brown and R. F. McFarlin, Am. Soc. *78*, 252 (1956).

[23] W. D. Emmons and J. P. Freeman, Am. Soc. *77*, 4415 (1955).

[24] T. L. Cairns and B. E. Englund, J. Org. Chem. *21*, 140 (1956).

[25] J. H. Brewster and C. J. Ciotti, Jr., Am. Soc. *77*, 6214 (1955).

There is a new publication on a synthesis of hydroperoxides which has previously been described in Volume *9*, (*9*, 337; Am. Soc. *77*, 6032 (1955)). The research of Emmons and coll. on trifluoroperacetic acid as an oxidizing agent (cf. *9*, 169; *10*, 146/7) has yielded an excellent method for the epoxidation of carbon-carbon double bonds[27].

New data about nitrogen compounds include two ways of alkylating amines, one with alcohols in the presence of a nickel catalyst[28], the other with phosphates and phosphonates[29]; and two methods for the preparation of hydrazines, one with chloramine (*10*, 252), the other through sydnones (*10*, 37; Am. Soc. *77*, 6604 (1955)). Aliphatic nitro compounds have been made by nitration in the presence of polyphosphoric acid[30] and by oxidation of oximes with trifluoroperacetic acid[31]. An interesting alkaline nitration method uses cyanohydrin nitrates as reagents[32].

Derivatives containing the azo group are occasionally described in the current literature. These derivatives are useful for separating, by chromatography, compounds originally non-colored, e. g. alcohols[33] or conjugated dienes[34].

The synthesis of homologous α-hydroxycarboxylic acids from carboxylic acids[35] illustrates the promising reaction of diazomethyl ketones with sulfenyl chlorides.

Perfluoroalkane derivatives can be prepared by electrolysis in anhydrous hydrofluoric acid[36]. Silver trifluoroacetate has been recommended for iodinations[37].

Because it does not require the use of a basic catalyst, a new method of phosphorylation is particularly suitable for base-sensitive compounds[38]. Phosphonic acids can be made from quaternary ammonium salts[39].

---

[26] C. R. Hauser and D. S. Hoffenberg, J. Org. Chem. *20,* 1448 (1955).

[27] W. D. Emmons and A. S. Pagano, Am. Soc. *77,* 89 (1955).

[28] Synth. Meth. *10,* 337; L. T. Plante and L. B. Clapp, J. Org. Chem. *21,* 86 (1956).

[29] A. and C. C. Barker, Soc. *1953,* 2034; T. L. Fletcher, M. E. Taylor, and A. W. Dahl, J. Org. Chem. *20,* 1021 (1955).

[30] J. P. Kispersky and K. Klager, Am. Soc. *77,* 5433 (1955).

[31] W. D. Emmons and A. S. Pagano, Am. Soc. *77,* 4557 (1955).

[32] W. D. Emmons and J. P. Freeman, Am. Soc. *77,* 4387, 4391 (1955).

[33] E. O. Woolfolk, F.-E. Beach, and S. P. McPherson, J. Org. Chem. *20,* 391 (1955).

[34] P. Nayler and M. C. Whiting, Soc. *1955,* 2970.

[35] F. Weygand and H. J. Bestmann, Z. Naturf. *10b,* 296 (1955); B. *88,* 1988 (1955).

[36] T. Gramstad and R. N. Haszeldine, Soc. *1956,* 173.

[37] Synth. Meth. *7,* 562; D. E. Janssen, J. VanAllan, and C. V. Wilson, J. Org. Chem. *20,* 1326 (1955).

The three formic C-atoms derived from the decomposition of 1.3.5-triazine have been used to make formamidines and related 1.3-heterocyclics[40]. Taylor and coll. ingeniously synthesized pteridines by reclosing, with properly chosen reactants, pyrazine intermediates which had been obtained by ring opening of readily available pteridines[41].

The cleavage of the carbon-carbon double bond can be carried out in such a way that two alcohols are formed (*10*, 149). The carbohydrate degradation via sulfones has proved to be an excellent method (*9*, 342; *10*, p. 193). The degradation of α-halogenocarboxylic acids to ethylene derivatives has been extended in scope (*8*, 944; *10*, p. 555).

Biochemical oxidation has been used to produce unsatd. steroid derivatives[42] and epoxy steroids from unsatd. steroids[43].

Syntheses for several important compounds have been described, as follows: A preparation of aldosterone[44]; a good synthesis of pteroylglutamic acid[45]; a purine synthesis in which formamide is used, first as a solvent, then as a reactant[46]; and finally a convenient azulene synthesis[47].

Tungsten disulfide has been recommended for the hydrogenolysis of oxygen-containing compounds (*10*, 106). Rhodium has been introduced as a catalyst[48]. 3,5-Dialkyl-4-piperidones have been obtained from 3,5-dialkylidene-4-piperidones with palladium-on-carbon in ethylene glycol (*10*, 553; cf. *9*, 5). Lithium in aliphatic amines has been found to be particularly well suited for the selective reduction of ar. hydrocarbons to monoolefins[49]. Sodium dispersions have been used in a variety of reactions[50]. Bergmann and coll. have begun a study of the use of basic ion exchange resins as catalysts in the Michael reaction[51].

---

[38] R. W. Chambers, J. G. Moffatt, and H. G. Khorana, Am. Soc. *77*, 3416 (1955).

[39] T. C. Myers, R. G. Harvey, and E. V. Jensen, Am. Soc. *77*, 3101 (1955).

[40] C. Grundmann and A. Kreutzberger, Am. Soc. *77*, 6559 (1955).

[41] E. C. Taylor, Jr., R. B. Garland, and C. F. Howell, Am. Soc. *78*, 210 (1956).

[42] J. Fried, R. W. Thoma, and A. Klingsberg, Am. Soc. *75*, 5764 (1953); E. Vischer, C. Meystre, and A. Wettstein, Helv. *38*, 1502 (1955).

[43] B. M. Bloom and G. M. Shull, Am. Soc. *77*, 5767 (1955).

[44] J. Schmidlin et al., Experientia *11*, 365 (1955).

[45] M. Sletzinger et al., Am. Soc. *77*, 6365 (1955).

[46] H. Bredereck and A. Edenhofer, B. *88*, 1306 (1955).

[47] K. Hafner and K. Ziegler, Ang. Ch. *67*, 301 (1955).

[48] Synth. Meth. *10*, 76; L. D. Freedman, G. O. Doak, and E. L. Petit, Am. Soc. *77*, 4262 (1955).

[49] R. A. Benkeser et al., Am. Soc. *77*, 3230, 6042 (1955).

[50] Synth. Meth. *10*, 571; J. F. Nobis and L. F. Moormeier, Ind. Eng. Chem. *46*, 539 (1954); C. E. Frank and W. E. Foster, Ind. Eng. Chem. *46*, 1019 (1954); C. S. Rondestvedt, Jr., and I. Nicholson, J. Org. Chem. *20*, 346 (1955).

As to solvents, new uses have been found for methyl Cellosolve[52]; methylal has been recommended for reductions with lithium aluminum hydride[53].

The following references, contained in Vol. 9 under Trends, have been entered in this volume[54]:

2/545; 7/49, 57, 67, 77, 81, 123; 8/223; 9/219; 10/299; 12/405; 13/321; 14/103, 104; 16/391; 17/176; 18/582; 19/24; 20/107; 21/85; 22/55; 23/629; 24/177; 26/226; 27/234; 28/257; 29/192; 30/185; 31/174; 35/250, 607; 36/436; 37/428; 38/453; 39/475; 40/470; 41/628; 42/630; 43/593; 44/381; 45/639; 47/125; 48/681; 49/113; 50/416, 701; 53/373, 648; 55/202; 56/34.

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[51] E. D. Bergmann and R. Corett, J. Org. Chem. *21,* 107 (1956).

[52] e. g. M. Sletzinger et al., Am. Soc. *77,* 6365 (1955).

[53] E. Bernatek, Acta Chem. Scand. *8,* 874 (1954).

[54] The first figure refers to the footnote in Trends, Vol. 9, the second figure to the entry number in this volume.

Formation of H—O Bond

Uptake

Addition to Oxygen HO ⇓ OO

Phenyl magnesium bromide C_6H_5MgBr

Hydroxy compounds from peroxides ←

s. *6*, 1

Lithium aluminum hydride $LiAlH_4$

Diols from peroxides ⊂

s. *9*, 6

Addition to Oxygen and Carbon HO ⇓ OC

Potassium hydroxide/alcohol KOH

γ-Pyrone ring opening ⊂

s. *6*, 128

Zinc/acetic acid Zn/CH_3COOH

Quinols from quinones ←

s. *9*, 1

Lithium aluminum hydride $LiAlH_4$

2-Acylamino-3-aryl-2-propen-1-ols from azlactones ⊂

Reductive oxazolone ring opening

s. *9*, 2

Stannous chloride $SnCl_2$

Quinols from quinones ←

s. *7*, 1

Sulfur dioxide SO_2

s. *7*, 2

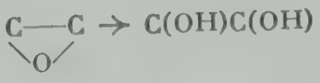
Sulfuric acid/acetic acid H_2SO_4/CH_3COOH

Hydroxycarboxylic acids from lactones ⊂

s. *6*, 2

Periodic acid HIO_4

Glycols from oxido compounds



$\underset{\diagdown O \diagup}{C—C} \rightarrow C(OH)C(OH)$

s. *7*, 3

Hydrochloric acid HCl

Hydroxycarbalkoxylactones from dilactones ⊂

s. *6*, 3

Nickel *Ni*

Quinols from quinones ←

s. *7*, 4

Platinum oxide *PtO_2*

s. *7*, 192

Rearrangement

Hydrogen/Carbon Type HO↶HC

Sodium/pyridine *Na/C_5H_5N*

Acetylene derivatives from benzofurans ⊂

s. *6*, 4

Potassium hydroxide/alcohol *KOH*

3-Keto-1,2-en-1-ols from β-diketones ←

s. *8*, 1

Acetic acid *CH_3COOH*

Quinols from enediones ←

s. *10*, 225

Stannous chloride *$SnCl_2$*

s. *6*, 5

Hydrochloric acid *HCl*

s. *7*, 5

Oxygen/Carbon Type HO↶OC

Without additional reagents *w.a.r.*

Tropolones by enolization CHCO→C:C(OH)

s. *9*, 3

Sodium hydroxide *NaOH*

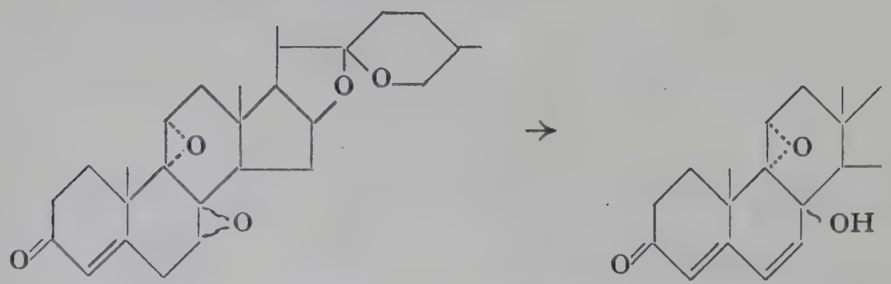
Ethylenecarboxylic acids from lactones ⊂

s. *7*, 6

Potassium hydroxide *KOH*

Partial formation of 2-ethylenealcohols from oxido compounds

1.



A mixture of 7ξ,8ξ:9α,11α-diepoxy-Δ⁴-22a-spirosten-3-one, KOH, ethanol, and some water allowed to stand 50 min. at room temp., the course of the rearrangement being followed spectrophotometrically → $9\alpha,11\alpha$-epoxy-$\Delta^{4,6}$-22a-spirostadien-8ξ-ol-3-one. Y: ca. 100%. A. J. Lemin and C. Djerassi, Am. Soc. *76*, 5672 (1954).

Sodium/alcohol *NaOR*

Ethylenealcohols from cyclic ethers
s. *7*, 744

Potassium cyanide *KCN*

Ethylenecarboxylic acids from phthalides
s. *8*, 2

Pyridine C_5H_5N

Pentad-enols ←
s. *7*, 7

Sulfuric acid H_2SO_4

Hydroxynaphthoquinones from oxidonaphthoquinones ←
s. *7*, 8

Hydrobromic acid *HBr*

Tropolones from cyclic diene-α-diones ←
Phenol acetates from dienones
s. *9*, 4

Palladium-carbon *Pd-C*

s. *9*, 5

Sulfur/Carbon Type HO⤺SC

Potassium hydroxide *KOH*

Sulfinic acids from cyclic sulfones C
s. *10*, 691

Exchange

Hydrogen ↑ HO⇅H

Via intermediates *v.i.*

Carboxylic acids-D from carboxylic acids COOH → COOD
s. *8*, 134a

Oxygen ↑ HO⇅O

Sodium *Na*

Alcohols from peroxides R·OO·R → 2 R·OH
s. *7*, 9

Lithium aluminum hydride $LiAlH_4$

Alcohols from alkyl- and acyl peroxides ←
Diols from photoöxides
s. *9*, 6

Nitrogen ↑ HO ⇅

Sodium hydroxide *NaO*

Selective hydrolysis of nitric acid esters $ONO_2 \rightarrow O$

s. *8*, 416

Lithium aluminum hydride *LiAlH*

Alcohols from nitric and nitrous acid esters ←

s. *8*, 3

Sodium sulfide Na_2S

Cleavage of carbohydrate nitrates $ONO_2 \rightarrow OH$

s. *9*, 7

Halogen ↑ HO ⇅ Hal

Sodium *Na*

Ethylenealcohols from cyclic halogenethers
Synthesis with addition of 4 and 5 C-atoms

s. *6*, 6

Butylsodium C_4H_9Na

Acetylenealcohols from cyclic halogenethers

s. *9*, 8

Sodium amide $NaNH_2$

s. *9*, 9

Sodium sulfite Na_2SO_3

Sulfinic acids from sulfonic acid chlorides $SO_2Cl \rightarrow SO_2H$

s. *10*, 476

Lithium aluminum hydride $LiAlH_4$

s. *8*, 4

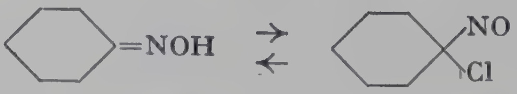
Sodium sulfide Na_2S

s. *6*, 7

Platinum oxide PtO_2

Oximes from 1,1-nitroso chlorides
and reverse reaction ←

2.



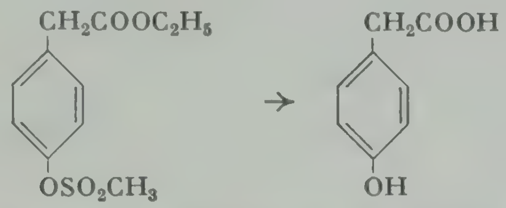
Chlorine passed into an ethereal soln. of cyclohexanone oxime in the dark with stirring until an initially formed precipitate has again dissolved and the blue color assumes a green shade → 1-chloro-1-nitrosocyclohexane (Y: 83%) hydrogenated with PtO_2 in ethyl acetate until the color disappears, and the resulting hydrochloride treated with NaOH → cyclohexanone oxime (Y: 86%). F. e. and reduction reagents s. E. Müller, H. Metzger, and D. Fries, B. *87*, 1449 (1954).

Sulfur ↓ HO⇅S

Sodium hydroxide *NaOH*

Demesylation $OSO_2CH_3 \rightarrow OH$

3.



Ethyl p-methanesulfonoxyphenylacetate refluxed 2 hrs. with 10%-NaOH → p-hydroxyphenylacetic acid. Y: 82%. **Stability of the mesyl protective group** s. J. H. Looker and D. N. Thatcher, J. Org. Chem. *19*, 784 (1954).

Potassium hydroxide *KOH*

Selective detosylation OTs → OH
s. *6*, 8

Sodium acetate CH_3COONa

Demesylation $OSO_2CH_3 \rightarrow OH$
Walden inversion of acylaminosugars
s. *9*, 10

Lithium aluminum hydride $LiAlH_4$

Cleavage of p-toluenesulfonic acid esters, with simultaneous formation of hydrocarbons from p-toluenesulfonic acid esters and alcohols from oxido compounds ←
s. *8*, 90

Sulfuric acid H_2SO_4

Hydrolysis of sulfuric acid esters $OSO_3^- \rightarrow OH$
s. *9*, 176

Hydrochloric acid *HCl*
s. *8*, 883; *9*, 203

Nickel *Ni*

Cleavage of sulfonic acid esters $ROSO_2R' \rightarrow ROH$
s. *6*, 9

Remaining Elements ↓ HO⇅Rem

Without additional reagents *w.a.r.*

Cleavage of boron complex salts ←
s. *8*, 802

Hydrochloric acid *HCl*

Hydrolysis of phosphoric acid esters $\cdot OPO(OH)_2 \rightarrow \cdot OH$
s. *6*, 10

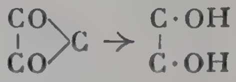
Carbon ↑ HO⇅C

Without additional reagents *w.a.r.*

Cleavage of ethers
with simultaneous formation of
ethylene derivatives from acoxy compounds ROR → ROH
s. *8*, 881

Cleavage of acetals ←
s. *10*, 220

Cleavage of isopropylidene derivatives
of carbohydrates s. *10*, 161



O-Dealkylation of alkoxysilanes ←

4. $(CH_3)_2Si(OCH_3)_2 \rightarrow (CH_3)_2Si(OH)_2$

A mixture of dimethyldimethoxysilane (prepn. s. 129) and excess distilled water refluxed 10 min. with careful exclusion of traces of acid or alkali → dimethylsilanediol. Y: 65-78%. F. e. s. S. W. Kantor, Am. Soc. *75*, 2713 (1953).

Hydroxylamines from N-oxides ←
s. *7*, 10; s. a. M. A. T. Rogers, Soc. *1955*, 769

Sodium hydroxide *NaOH*

Cleavage of ethers ROR → ROH
s. *6*, 11

Deacetylation OAc → OH
s. *7*, 129; *8*, 165

α-Hydroxyketones from 1-acoxy-1,2-oxido compounds
s. *7*, 184

Partial hydrolysis of steroid-3-acoxy groups
s. *8*, 5

Selective hydrolysis
s. *7*, 11

Hydroxyacetals from acoxyacetals
Protection of hydroxyl groups
s. *9*, 11

Selective O-deacetylation
s. *8*, 771; also total deacetylation s. F. C. Uhle and S. H. Robinson, Am. Soc. *77*, 3544 (1955)

Carboxylic acids from carboxylic acid esters COOR → COOH
s. *8*, 264, 288; *9*, 44

Hydroxymethylenecarboxylic acids
s. *7*, 869

Partial hydrolysis
s. *7*, 13

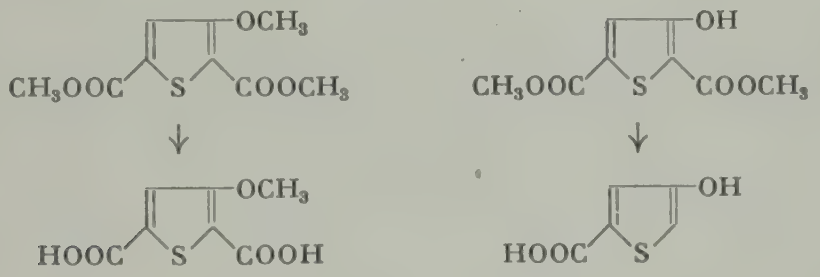
Selective hydrolysis
s. *6*, 137; *9*, 12; *10*, 368

Alkoxycarboxylic acids
from alkoxycarboxylic acid esters
s. *8*, 267

N-Carbobenzoxypeptides from
N-carbobenzoxypeptide esters
s. *8*, 6

Carboxylic acids from carboxylic acid esters,
also with simultaneous decarboxylation

5.



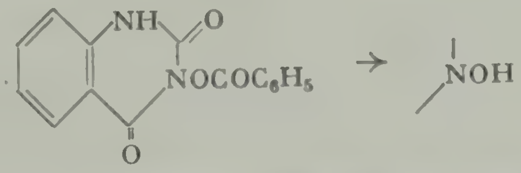
3-Methoxy- | 3-Hydroxy-
2.5-dicarbomethoxythiophene refluxed 1 hr. with 2 *N* NaOH →
3-methoxy-2,5-dicarboxythiophene. Y: 80%. | 3-hydroxy-5-carboxythiophene. Y: 81%.

H. Fiesselmann, P. Schipprak, and L. Zeitler, B. *87*, 841 (1954).

Hydroxyketones from lactolesters ←
s. *7*, 12

N-Hydroxy- from N-acoxy compounds NOAc → NOH
Selective hydrolysis

6.



3-Benzoxy-1H-quinazolinedione dissolved in warm 5%-NaOH, and heated 20 min. on a steam bath → 3-hydroxy-1H-quinazolinedione. Y: 99%. C. D. Hurd, C. M. Buess, and L. Bauer, J. Org. Chem. *19*, 1140 (1954).

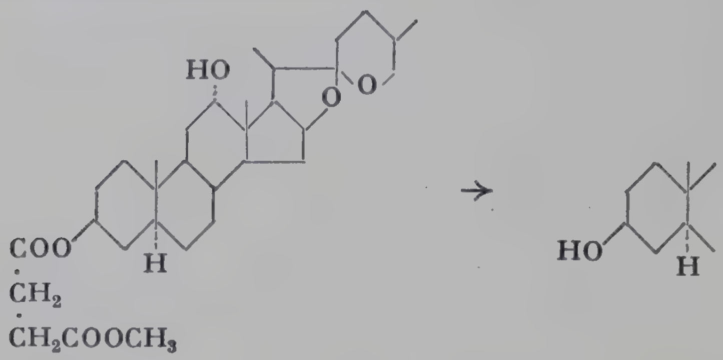
Sodium hydroxide/potassium hydroxide *NaOH/KOH*

Cleavage of ethers ROR → ROH
s. *6*, 160

Potassium hydroxide *KOH*

Cleavage of succinoxy derivatives OAc → OH

7.



A soln. of 12-epi-rockogenin 3-methyl succinate in tetrahydrofuran-methanol (1:1) refluxed 2.5 hrs. with aq. 8%-KOH, and allowed to stand overnight at room temp. ⟶ 12-epi-rockogenin. Y: ca. 100%. R. Hirschmann et al., Am. Soc. *76*, 4013 (1954).

Partial deacetylation of steroids
s. *9*, 13

Carboxylic acids from carboxylic acid esters COOR → COOH
s. *6*, 136, 689; *9*, 159

Saponification of β-ketocarboxylic acid esters
s. *8*, 7

Polycarboxylic acids from polycarboxylic acid esters
Mild hydrolysis
s. *9*, 14

Partial hydrolysis
s. *8*, 8

Isomeric dicarboxylic acid monoesters
s. *8*, 229

Selective hydrolysis
s. *6*, 12

Sodium hydroxide/alcohol *NaOH/ROH*
s. *6*, 466

Potassium hydroxide/alcohol *KOH/ROH*

Cleavage of ethers ROR → ROH
s. *8*, 9

Deacetylation OAc → OH
s. *8*, 10

Hydroxymercaptals from acoxymercaptals
Selective hydrolysis
s. *9*, 15

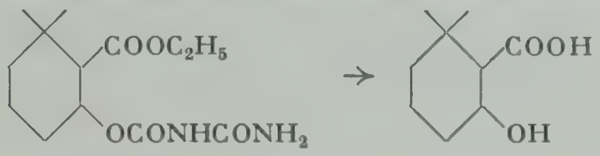
α-Hydroxyketones from 1-acoxy-1,2-oxido compounds ←
s. *9*, 202

Carboxylic acids from carboxylic acid esters COOR → COOH
s. *9*, 892; *10*, 246

Partial hydrolysis
s. *7*, 13

Cleavage of allophanates ←
with simultaneous hydrolysis of carboxylic acid esters

8.



Ethyl 1,1-dimethyl-3-hydroxycyclohexyl-2-carboxylate allophanate heated 3 hrs. with alc. KOH on a water bath → ethyl 1,1-dimethyl-3-hydroxycyclohexyl-2-carboxylic acid. Y: 86%. G. Gamboni, H. Schinz, and A. Eschenmoser, Helv. *37*, 964 (1954).

Silanols from alkoxysilanes SiOR → SiOH
s. *7*, 14

Sodium/alcohol *NaOR*

Deacetylation OAc → OH
s. *6*, 13

of carbohydrates
s. *9*, 229

of glycosides
s. *7*, 15

Partial hydrolysis of steroid-3-acoxy groups
s. *8*, 11

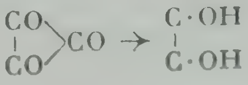
Barbituric acids with simultaneous deacetylation
s. *7*, 441

Hydroxyphosphoric acid esters
from acetoxyphosphoric acid esters
s. *6*, 14

Directed interesterification ←
Modified Eckey process
Single-fatty acid 1,3-diglycerides
s. *7*, 16

Hydroxyquinones from triacoxyisocyclics ←
s. *6*, 15

Cleavage of carbohydrate carbonates
s. *6*, 16


$\begin{matrix}CO\\|\\CO\end{matrix}\!\!>CO \rightarrow \begin{matrix}C\cdot OH\\|\\C\cdot OH\end{matrix}$

Sodium/liq. ammonia *Na/NH₃*

Partial cleavage of methyl ethers ROR → ROH
s. *9*, 16

Sodium carbonate Na_2CO_3

Hydrolysis of formoxy compounds $OCHO \rightarrow OH$
s. *8*, 159

Partial O-deacetylation $OAc \rightarrow OH$
s. *9*, 267

Alkoxycarboxylic acids
from alkoxycarboxylic acid esters $COOR \rightarrow COOH$
s. *8*, 273

Sodium hydrogen carbonate $NaHCO_3$

Hydroxymethylene from
alkoxymethylene compounds $C{:}CHOR \rightarrow C{:}CHOH$
s. *8*, 12

Potassium carbonate K_2CO_3

Carboxylic acids from carboxylic acid esters $COOR \rightarrow COOH$
Selective hydrolysis
s. *7*, 17

Potassium hydrogen carbonate $KHCO_3$

Masking of hydroxyl groups $OCHO \rightarrow OH$
Selective hydrolysis of formoxy compounds
s. *9*, 17

Lithium chloride $LiCl$

Monodebenzylation of phosphoric acid esters $OCH_2C_6H_5 \rightarrow OH$
s. *7*, 18; cf. M. Miyano, Am. Soc. *77*, 3524 (1955)

Sodium chloride/aluminum chloride s. $NaCl/AlCl_3$
Aluminum chloride/sodium chloride

Potassium iodide/phosphoric acid s. KI/H_3PO_4
Phosphoric acid/potassium iodide

Ammonia NH_3

Selective deacylation $OAc \rightarrow OH$
s. *7*, 56; *8*, 18

Ammonia NH_3

Deacetylation
s. *8*, 383

Aminoalcohols from acoxyhalides
s. *7*, 483

Triton B

←

Carboxylic acids from carboxylic acid esters $COOR \rightarrow COOH$
Cinnamylidenemalonic acids
s. *9*, 828

Piperidine $C_5H_{11}N$

Selective hydrolysis – Debenzoylation $OBz \rightarrow OH$
s. *6*, 17

N-Methylmorpholine ←

Partial debenzylation of phosphoric acid esters $OCH_2C_6H_5 \rightarrow OH$

s. *6*, 18

Magnesium hydroxide *$Mg(OH)_2$*

Aldehydes from 1,1-di(acoxy) compounds $CH(OAc)_2 \rightarrow CHO$

s. *6*, 19

Alkylmagnesium halide *RMgHal*

Deacetylation $OAc \rightarrow OH$

s. *6*, 20

Magnesium sulfate/palladium-strontium carbonate *$MgSO_4/Pd\text{-}SrCO_3$*

s. Palladium-strontium carbonate/magnesium sulfate

Barium hydroxide *$Ba(OH)_2$*

Dicarboxylic acid monoesters
from dicarboxylic acid esters $COOR \rightarrow COOH$

s. *7*, 19; s. a. K. Mislow and J. V. Steinberg, Am. Soc. *77*, 3807 (1955)

Partial hydrolysis of phosphoric acid esters ←

s. *9*, 189

Barium methoxide *$Ba(OR)_2$*

Deacylation of glycosides $OAc \rightarrow OH$

s. *6*, 291

Debenzoylation s. *8*, 253

Selective hydrolysis
Deacetylation of carbohydrates

s. *8*, 13

Lithium aluminum hydride *$LiAlH_4$*

Cleavage of β-oxypropionitriles $ROR \rightarrow ROH$

9. $C_6H_5OCH_2CH_2CN \rightarrow C_6H_5OH$

β-Phenoxypropionitrile allowed to react with excess $LiAlH_4$ in tetrahydrofuran at 65° → phenol. Y: 99.3%. F. e. s. L. M. Soffer and E. W. Parrotta, Am. Soc. *76*, 3580 (1954).

Deacylation – Optically active compounds $OAc \rightarrow OH$

s. *7*, 20

Boric acid *HBO_2*

Selective hydrolysis of acetals ←

Monoglycerides s. *9*, 18

Aluminum chloride *$AlCl_3$*

Cleavage of ethers $ROR \rightarrow ROH$

s. *10*, 103

Aluminum chloride/sodium chloride *$AlCl_3/NaCl$*

s. *6*, 21

Aluminum bromide *$AlBr_3$*

Selective hydrolysis
s. *7*, 21

Methyl alcohol *CH_3OH*

Methanolysis of trifluoroacetyl derivatives $OCOCF_3 \rightarrow OH$
Selective hydrolysis
s. *7*, 22

Yeast ←

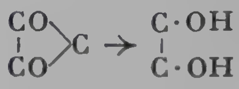
Disaccharides from trisaccharides ←
s. *9*, 19

Aspergillus oryzae enzyme ←

Cleavage of glycosides $ROR \rightarrow ROH$
s. *8*, 14

Amberlite ←

Cleavage of acetals – Carbohydrate derivatives
s. *7*, 23



Acetic anhydride/hydriodic acid *$(CH_3CO)_2O/HI$*
s. Hydriodic acid/acetic anhydride

Carboxylic acids and mercaptans ←

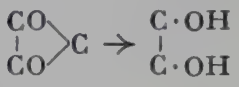
Acidolysis ←
s. *9*, 20

Formic acid *$HCOOH$*

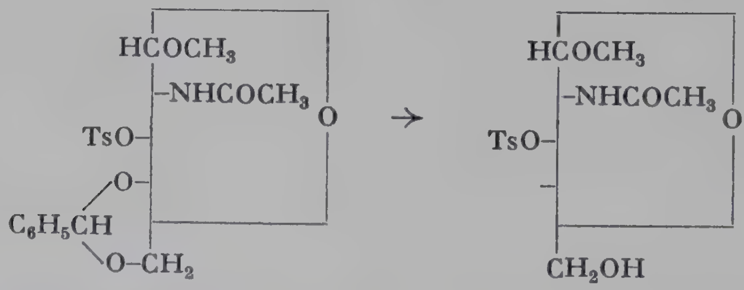
Carboxylic acids from carboxylic acid esters $COOR \rightarrow COOH$
s. *6*, 22

Acetic acid *CH_3COOH*

Cleavage of acetals
s. *9*, 303; *10*, 224



10.



Selective hydrolysis. A soln. of methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-p-toluenesulfonyl-α-D-galactopyranoside in glacial acetic acid heated 30 min. on a water bath while water is slowly added → methyl 2-acetamido-2-deoxy-3-O-p-toluenesulfonyl-α-D-galactopyranoside. Y: 86%. R. W. Jeanloz and P. J. Stoffyn, Am. Soc. *76*, 563, 555 (1954).

s. a. *9*, 21

Tartaric acid ←

Cleavage of sensitive acetals $C(OR)_2 \rightarrow CO$
Selective hydrolysis

11. $CH_3OCH_2[CH_2]_6CH(OCH_3)_2 \rightarrow CH_3OCH_2[CH_2]_6CHO$

A mixture of 1,1,8-trimethoxyoctane and satd. tartaric acid soln. shaken at intervals for 1 hr. → 8-methoxyoctanal. Y: 72%. F. e. s. C. D. Hurd and W. H. Saunders, Jr., Am. Soc. *74*, 5324 (1952); method s. G. Fischer and K. Löwenberg, A. *494*, 272 (1932).

Hypophosphorous acid/hydrobromic acid *H_3PO_2/HBr*
s. Hydrobromic acid/hypophosphorous acid

Phosphoric acid/potassium iodide *H_3PO_4/KI*

Hydroxycarboxylic acids ←
from alkoxycarboxylic acid esters
s. *7*, 24

p-Toluenesulfonic acid *TsOH*

Removal of protective groups ROR → ROH
Cleavage of tetrahydro-2-pyranyl ethers
s. *9*, 22

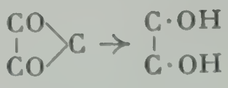
Carboxylic acids from carboxylic acid esters COOR → COOH
Labeled compounds s. *7*, 25

Sulfuric acid *H_2SO_4*

2-Hydroxy- from 2-alkoxy-benz-1,4-oxathienes OR → OH
s. *10*, 483

Partial cleavage of methyl ethers ROR → ROH
s. *9*, 23

Cleavage of acetals
s. *8*, 15

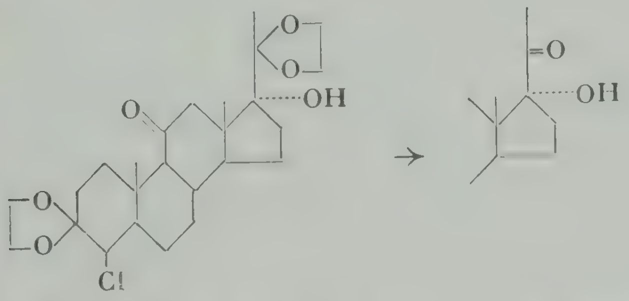


$$\begin{matrix}CO\\|\\CO\end{matrix}\!>\!C \rightarrow \begin{matrix}C\cdot OH\\|\\C\cdot OH\end{matrix}$$

Carbohydrate derivatives
s. *7*, 23; *8*, 313; s. a. P. A. J. Gorin, L. Hough, and J. K. N. Jones, Soc. *1955*, 582

Partial cleavage of steroid ketals

12.



1 drop of H_2SO_4 added to soln. of 4-chloro-17α-hydroxypregnane-3,11,20-trione 3,20-bis(ethylene ketal) in acetone-water, and allowed to

stand 24 hrs. → 4-chloro-17α-hydroxy-3,11,20-trione 3-ethylene ketal. Y: 79%.—The 3-ketal can only be removed by refluxing for prolonged periods. F. e. s. R. H. Levin et al., Am. Soc. *76*, 546 (1954).

Selective cleavage of acetals

13.

$$\mathrm{HOCH_2C(CH_3)_2CH(OH)CONHCH_2CH_2CONHCH_2CH(OC_2H_5)_2}$$
$$\downarrow$$
$$\mathrm{HOCH_2C(CH_3)_2CH(OH)CONHCH_2CH_2CONHCH_2CHO}$$

An aq. soln. of 1 g. 2-D-pantothenamidoacetaldehyde diethyl acetal acidified by adding 1 drop of 50%-H_2SO_4, then boiled 2 min. → 2-D-pantothenamidoacetaldehyde. Y: almost 100%. J. Baddiley and A. P. Mathias, Soc. *1954*, 2803.

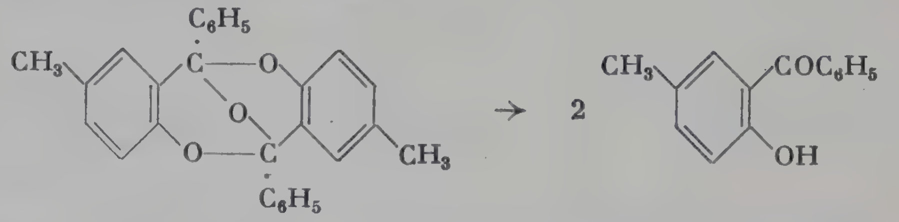
Cleavage of acetals and dehydration
s. *8*, 905

Aldehydes from 1,1-diacoxy compounds $CH(OAc)_2 \rightarrow CHO$
s. *9*, 251; *10*, 135

N-Alkylation of oxazolidiones
Blocking of carboxyl groups
by formation of tert-butyl esters
Hydrolysis of carboxylic acid esters COOR → COOH
under anhydrous conditions
s. *9*, 24

Epoxydioxocin ring opening C

14.



Finely powdered 6,12-diphenyl-2,8-dimethyl-6,12-epoxy-6H,12H-dibenzo[b,f][1,5]dioxocin dissolved at room temp. in concd. H_2SO_4, then diluted with water → 2-hydroxy-5-methylbenzophenone. Y: 91%. M. S. Newman and A. G. Pinkus, J. Org. Chem. *19*, 985 (1954); f. e. s. J. Org. Chem. *19*, 996.

Hydrochloric acid *HCl*

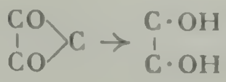
Cleavage of ethers ROR → ROH

Alcohols from alkoxymethyl ethers
s. *9*, 270

Selective hydrolysis
s. *8*, 16/7

Enols from enolethers C:C(OR) → C:C(OH)
s. *6*, 320

Cleavage of acetals
s. *6*, 575; *8*, 133; *9*, 318



of benzylidene derivatives of carbohydrates
s. *9*, 355

of alkyleneacetals
s. *6*, 216

Cleavage of formals —
s. *10*, 195

Oxo compounds from acetals $C(OR)_2 \rightarrow CO$
s. *9*, 665, 743, 903

α,β-Ethylenealdehydes from alkoxyacetals
s. *7*, 889

Selective hydrolysis
s. *6*, 23/4

Hydroxyoxo compounds from lactolides ←
s. *7*, 26

Selective O-deformylation $OCHO \rightarrow OH$
s. *10*, 481

Deacetylation $OAc \rightarrow OH$
s. *6*, 51; *7*, 27

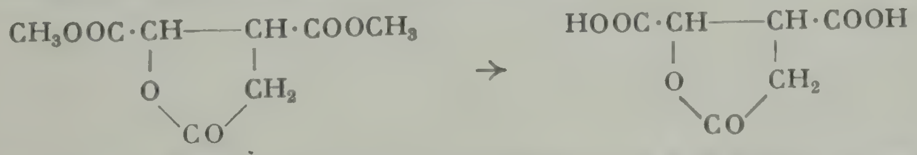
Carboxylic acids from carboxylic acid esters $COOR \rightarrow COOH$
Acidolysis
s. *6*, 25

Ethylenecarboxylic acids
from hydroxycarboxylic acid esters
s. *9*, 25

Dicarboxylic acid monoesters
from dicarboxylic acid diesters
Acidolysis
s. *9*, 27

Carboxylactones from carbalkoxylactones

15.



l-Isocitric lactone dimethyl ester boiled 6 hrs. in 3 *N* HCl → l-isocitric lactone. Y: 96%. H. B. Vickery, Biochem. Prep. *3*, 44 (1953).

Imidocarboxylic acids
from imidocarboxylic acid esters
s. *10*, 367

Selective hydrolysis

N-Thiocarbonylaminocarboxylic acids
s. *9*, 26

Optically active compounds
s. *6*, 26

Ring hydrogenation with subsequent removal of blocking groups $OCOOR \rightarrow OH$
s. *7*, 28

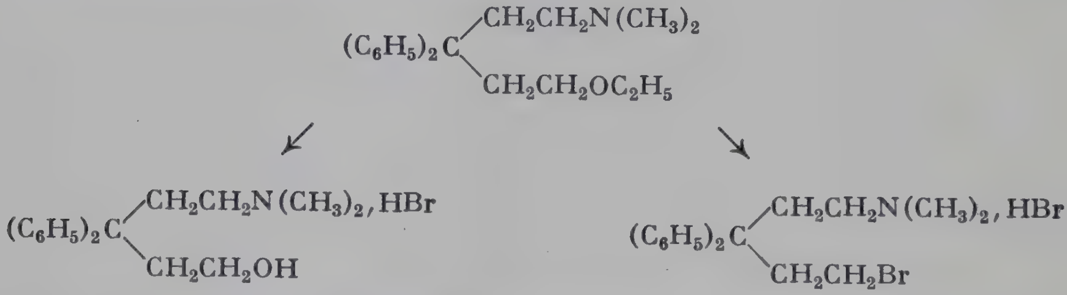
Silanols from alkoxysilanes $SiOR \rightarrow SiOH$
s. *7*, 14

Phosphinic acids from phosphinic acid esters $R_2POOR \rightarrow R_2POOH$
s. *7*, 659; s. a. Bochwic and J. Michalski, Rocniki Chem. *26*, 593 (1952)

Hydrobromic acid *HBr*

Alcohols and halides from ethers $ROR \rightarrow ROH$

16.



A soln. of 5-ethoxy-3,3-diphenyl-N,N-dimethylamylamine (prepn. s. 617) in 48%-HBr refluxed 22 hrs. → 5-hydroxy-3,3-diphenyl-N,N-dimethylamylamine hydrobromide. Y: 95%.—With a large excess of 48%-HBr, the 5-bromo analog is obtained in 71% yield. N. Sperber, M. Sherlock, and D. Papa, Am. Soc. *75*, 1122 (1953).

Cleavage of trityl ethers
s. *2*, 249; *3*, 10; s. a. J. L. Barclay, A. B. Foster, and W. G. Overend, Soc. *1955*, 2505

Hydrobromic acid/hypophosphorous acid *HBr/H_3PO_2*

Cleavage of methyl ethers
s. *9*, 28

Hydriodic acid *HI*

Cleavage of ethers
s. *6*, 27

Enols from enolethers $C{:}C(OR) \rightarrow C{:}C(OH)$
s. *6*, 320

Selective hydrolysis – Optically active compounds ←
s. *6*, 26

Carboxylic acids from hydrocarboxylic acid esters ←

Reductive hydrolysis

s. 7, 699

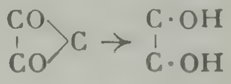
Hydriodic acid/acetic anhydride *$HI/(CH_3CO)_2O$*

Cleavage of methyl ethers ROR → ROH

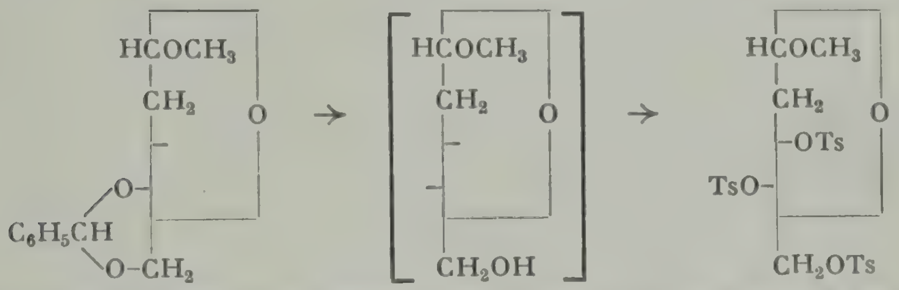
s. *9*, 29

Nickel *Ni*

Cleavage of acetals with subsequent tosylation



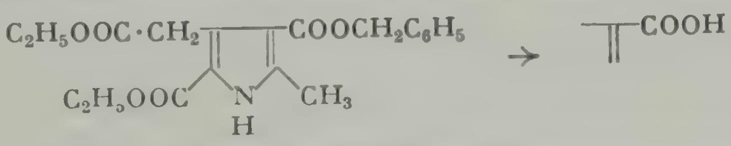
17.



Methyl 4.6-benzylidene-2-deoxy-α-D-guloside-(1,5) refluxed 2 hrs. with Raney-Ni, freshly prepared from Ni-Al-alloy at 50°, in 80%-alcohol, and the crude product allowed to stand 24 hrs. at 20° with p-toluenesulfonyl chloride in abs. pyridine ⟶ methyl 3,4.6-tritosyl-2-deoxy-α-D-guloside-(1,5). Y: 86%. H. R. Bolliger and T. Reichstein, Helv. *36*, 302 (1953).

Selective hydrogenolysis of carboxylic acid esters COOR → COOH

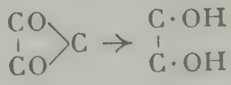
18.



Benzyl 5-carbethoxy-4-carbethoxymethyl-2-methylpyrrole-3-carboxylate hydrogenated 3 hrs. with Raney-Ni in abs. ethanol at 100°/100 atm. ⟶ 5-carbethoxy-4-carbethoxymethyl-2-methylpyrrole-3-carboxylic acid. Y: 91%. F. e. s. S. F. MacDonald, Soc. *1952*, 4176.

Alkaline nickel

Hydrocarbons from thioethers with simultaneous cleavage of acetals



s. *7*, 137

Palladium *Pd*

Hydrogenolysis of benzyl ethers ROR → ROH

s. 8, 289; *9*, 303

Debenzylation of carboxylic acid esters COOR → COOH

s. *7*, 62

Palladium-strontium carbonate/magnesium sulfate *$Pd\text{-}SrCO_3/MgSO_4$*

s. *7*, 827

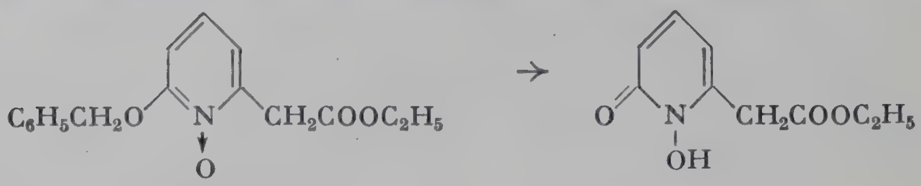
Palladium-carbon *Pd-C*

Hydrogenolysis of benzyl ethers ROR → ROH
s. *8*, 22; *9*, 303

of benzyl glycosides
Retention of configuration s. *7*, 29

1-Hydroxy-2-pyridones from 2-alkoxypyridine N-oxides ←

19.



A soln. of ethyl 2-benzyloxy-6-pyridylacetate 1-oxide in abs. ethanol shaken with 5%-Pd-on-charcoal until reduction is complete after ca. 45 min. → ethyl 1-hydroxy-2-pyridone-6-acetate. Y: 80%. F. e. s. R. Adams and S. Miyano, Am. Soc. *76*, 3168 (1954).

Hydrogenolysis of benzyl esters COOR → COOH
s. *7*, 30, 827; *8*, 741; *9*, 118, 434

Simultaneous cleavage
of carbobenzoxy derivatives of amines and benzyl esters
s. *9*, 860

Hydrogenolysis of phosphoric acid esters ←
s. *10*, 125

Platinum oxide *PtO_2*

Hydrogenolysis of phosphoric acid phenyl esters
s. *6*, 158; *7*, 31; s. a. J. Baddiley, J. G. Buchanan, and L. Szabó, Soc. *1954*, 3826

Platinum oxide and platinum oxide/palladium *PtO_2 and PtO_2/Pd*

Simultaneous removal of protective groups ←
Phosphoric acids from phosphoric acid esters
Cleavage of carbobenzoxy derivatives of amines
Aminophosphatides
s. *7*, 31

Via intermediates *v.i.*

Partial and selective deacylation of carbohydrates OAc → OH
via 1-chloro-2-trichloroacetyl derivatives
s. *8*, 18

Elimination

Oxygen ↑ **HO ⇑ O**

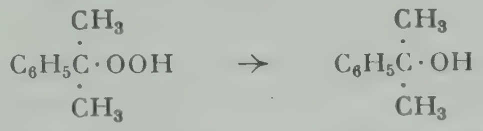
Without additional reagents *w.a.r.*

Carboxylic acids from peroxycarboxylic acids CO_2H → COOH
s. *7*, 241

Amines ←

Alcohols from hydroperoxides OOH → OH

20.



$$C_6H_5\overset{CH_3}{\underset{CH_3}{C}}\cdot OOH \rightarrow C_6H_5\overset{CH_3}{\underset{CH_3}{C}}\cdot OH$$

α,α-Dimethylbenzyl hydroperoxide heated 0.5 hr. with triethanolamine at 110-120° → α,α-dimethylbenzyl alcohol. Y: ca. 100%. F. e. and amines s. C. W. Capp and E. G. E. Hawkins, Soc. *1953*, 4106.

Zinc/acetic acid *Zn/CH$_3$COOH*

Ethylenealcohols from peroxides ↺

s. *9*, 30

Lithium aluminum hydride *LiAlH$_4$*

Hydroxy compounds from hydroperoxides OOH → OH

Alcohols

s. *7*, 32

Platinum *Pt*

s. *8*, 158

Platinum oxide *PtO$_2$*

s. *7*, 33

Formation of H—N Bond

Uptake

Addition to Oxygen and Nitrogen HN⇓ON

Zinc *Zn*

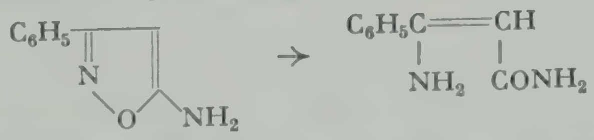
Reductive oxazine ring opening ↺

s. *6*, 28

Nickel *Ni*

Reductive isoxazole ring opening

21.



2 g. 5-amino-3-phenylisoxazole hydrogenated with Raney-Ni for 3 hrs. → 1.8 g. β-aminocinnamamide. F. e. s. G. Shaw and G. Sugowdz, Soc. *1954*, 665.

s. a. *8*, 19

Addition to Nitrogen HN⇓NN

Without additional reagents *w.a.r.*

Sulfonylhydrazonium salts from aminesulfonimides ←

s. *9*, 984

Electrolysis ↯
Hydrazines from diazonium salts $\overset{+}{N}_2 \rightarrow NHNH_2$
Flow electrolysis
s. *9*, 31

Phenylhydrazine $C_6H_5NHNH_2$
Hydrazo from azo compounds $N{:}N \rightarrow NHNH$
s. *9*, 41

Sodium hyposulfite $Na_2S_2O_4$
o-Aminoazo compounds from 1,2,3-triazolium salts ↺
s. *6*, 29

Addition to Nitrogen and Carbon HN⇓NC

Electrolysis ↯
Medium-N-heterocyclic alcohols from N-bicyclic ketones ↺
s. *9*, 32

Platinum oxide PtO_2
Arylenedi(sulfonamides) ←
from quinone di(sulfonimides)
s. *7*, 512

Rearrangement

Hydrogen/Oxygen Type HN↶HO

Sulfur/sulfuric acid S/H_2SO_4
α,β-Ethylenecarboxylic acid amides $CHC(OH)CN \rightarrow C{:}C{\cdot}CONH_2$
from cyanohydrins
s. *6*, 30

Exchange

Oxygen ↑ HN⇵O

Electrolysis ↯
α-Aminocarboxylic acids $C{:}NOH \rightarrow CHNH_2$
from α-oximinocarboxylic acids
s. *8*, 524

Zinc Zn
Acylamines from oximes $C{:}NOH \rightarrow CHNHAc$
s. *8*, 20; s. a. H. Hellmann and F. Lingens, H. *297*, 283 (1954)

Acylamines from nitro compounds $NO_2 \rightarrow NHAc$
s. *9*, 33

Hydroxylamines from nitro compounds $NO_2 \rightarrow NHOH$
s. *2*, 265; s. a. Helv. *37*, 1885 (1954)

Zinc/mercuric chloride *$Zn/HgCl_2$*
α-Acylaminoketones from α-isonitrosoketones C:NOH → CHNHAc
s. *7*, 34

Lithium aluminum hydride *$LiAlH_4$*
Prim. amines from oximes C:NOH → $CHNH_2$
s. *7*, 35; 2-aryloxyamines s. M. Kopp, Bl. *1954*, 628

Amines from nitroethylene derivatives ←
s. *6*, 87

Unsym. hydrazines and amines from N-nitrosamines ←
s. *9*, 34; hydrazines s. a. C. G. Overberger et al., Am. Soc. *77*, 4100 (1955)

Tin *Sn*
Amines from nitro compounds NO_2 → NH_2
s. *6*, 31

Stannous chloride *$SnCl_2$*
s. *2*, 41/2; s. a. R. C. Elderfield et al., Am. Soc. *77*, 4816 (1955)

Hydrazine/potassium hydroxide *$H_2N{\cdot}NH_2/KOH$*
with simultaneous reduction of oxo to hydrocarbon groups
s. *9*, 123

Hydrazine/nickel s. Nickel/hydrazine *$H_2N{\cdot}NH_2/Ni$*

Sodium sulfide *Na_2S*
Diamines from quinone dioximes ←
s. *7*, 117

Ammonium sulfide *$(NH_4)_2S$*
Amines from nitro compounds NO_2 → NH_2
s. *6*, 32

Sodium hydrogen sulfide *NaHS*
Aminoazo from nitroazo compounds
s. *9*, 35

Partial reduction of polynitro compounds
s. *2*, 38; s. a. E. R. Ward and T. M. Coulson, Soc. *1954*, 4545

Hydrosulfite *$S_2O_4^{--}$*
Amines from nitroso compounds NO → NH
s. *8*, 245

Iron *Fe*
Amines from nitro compounds NO_2 → NH_2
s. *6*, 820; *7*, 78

simultaneously: amines from N-oxides
s. *6*, 389

in benzene
selective reduction s. *7*, 37; halogenamines s. R. B. Carlin and E. A. Swakon, Am. Soc. *77*, 966 (1955); method s. S. E. Hazlet and G. A. Dornfeld, Am. Soc. *66*, 1781 (1944)

Ferrous sulfate/ammonia *$FeSO_4/NH_3$*

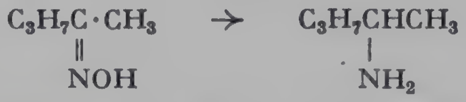
Ethyleneamines from nitroethylene derivatives
s. *7*, 38

Ferrous sulfate/barium hydroxide *$FeSO_4/Ba(OH)_2$*
s. *6*, 33

Nickel *Ni*

Prim. amines from oximes C:NOH → CHNH$_2$

22.



$$\underset{\displaystyle NOH}{C_3H_7\overset{}{C}\cdot CH_3} \rightarrow \underset{\displaystyle NH_2}{C_3H_7CHCH_3}$$

Low pressure hydrogenation. A soln. of 2-pentanone oxime in 95%-ethanol hydrogenated with Raney-Ni at room temp. and an initial pressure of 3 atm. until the theoretical amount of H_2 has been absorbed → 2-aminopentane. Y: 85%. F. e. s. D. C. Iffland and Teh-Fu Yen, Am. Soc. *76*, 4180 (1954).

from ketones via oximes
s. *9*, 36

Aminophenols from nitrosophenols NO → NH$_2$
s. *10*, 287

5-Amino- from 5-nitrosopyrimidines
s. *9*, 448

Amines from nitro compounds NO_2 → NH_2
s. *8*, 123

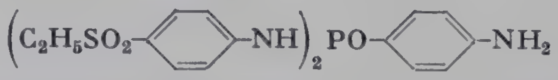
Aliphatic compounds
s. *7*, 39

Selective reduction
s. *7*, 40

Aminoacetals from nitroacetals
s. *6*, 34

Aminohydroxycarboxylic acids
s. *7*, 41

23.



Amino-sulfonyl-phosphonic acid diamides. A soln. of N,N′-bis-(p-ethylsulfonyl-phenyl)-P-(p-nitrophenyl)phosphonic diamide (prepn. s. 259) in abs. alcohol-acetone hydrogenated with Raney-Ni at an initial pressure of 40 lb. until the H_2-absorption practically ceases → N,N′-bis-(p-ethylsulfonylphenyl)-P-(p-aminophenyl)phosphonic diamide. Y: 84%. F. e. s. G. O. Doak and L. D. Freedman, Am. Soc. *76*, 1621 (1954); aminosulfones s. a. I. Kh. Fel'dman and E. S. Nikitskaya, Ж. *19*, 134 (1949); C. A. *43*, 6179i; B. R. Baker, M. V. Querry, and A. F. Kadish, J. Org. Chem. *15*, 402 (1950); with PtO_2 s. D. F. Elliott and C. Harington, Soc. *1949*, 1374.

α-Acylamino-α,β-ethylenecarboxylic acid esters from α-nitro-α,β-ethylenecarboxylic acid esters $NO_2 \rightarrow NHAc$
in large batches s. 7, 42

Amidrazones from 1,1-nitroaldehyde hydrazones $NO_2 \rightarrow NH_2$
s. *8*, 21; s. a. B. *88*, 1284 (1955)

Nickel/hydrazine *Ni/H₂N·NH₂*

Amines from nitro compounds
s. *9*, 37

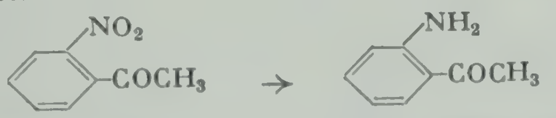
Nickel formate-paraffin ←

Catalytic reduction in aqueous soln.
s. *7*, 43

Nickel, platinized *Ni/Pt*
s. *7*, 44

Palladium/cyclohexene *Pd*

24.



Transfer-hydrogenation.—Selective hydrogenation. With Pd as catalyst and cyclohexene as donor, carbon-carbon double and triple bonds, nitro-, azomethine-, azo-, azoxy groups, and some halogen compounds undergo hydrogenation, reduction, or hydrogenolysis, whereas cyano and carbonyl groups (except in quinones and α-diketones) do not react. Other functional groups remaining unchanged are hydroxyl, alkoxyl, and carboxyl. Transfer-hydrogenation is often remarkably selective and affords higher yields than direct catalytic hydrogenation or other methods of reduction. The ease of transfer-hydrogenation can be very sensitive to structure variations in the acceptor.—E: o-Nitroacetophenone, Pd-black, and cyclohexene in ethanol refluxed 17 hrs. → o-aminoacetophenone. Y: 95%. E. A. Braude, R. P. Linstead et al., Soc. *1954*, 3586, 3578, 3595; s. a. Y. Ahmad and D. H. Hey, Soc. *1954*, 4516.

Palladium-strontium carbonate and palladium-barium sulfate *Pd-SrCO₃ and Pd-BaSO₄*

Aminonitriles
s. 7, 474

Palladium-barium sulfate *Pd-BaSO₄*

also with simultaneous replacement of chlorine by hydrogen
s. *6*, 35

Amidrazones from 1,1-nitroaldehyde hydrazones
s. *8*, 21

Palladium-barium sulfate/oxalic acid *$Pd\text{-}BaSO_4/(COOH)_2$*
Aliphatic hydroxylamines from aliphatic nitro compounds $NO_2 \rightarrow NHOH$
s. *6*, 36

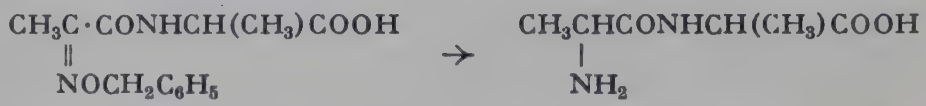
Palladium-carbon *Pd-C*
Amines from alkoxylamines $>NOR \rightarrow >NH$
s. *7*, 45

α-Aminoketones from α-isonitrosoketones $C{:}NOH \rightarrow CHNH_2$
s. *9*, 38

α-Aminoalcohols from α-isonitrosoketones $COC{:}NOH \rightarrow CH(OH)CHNH_2$
Stereospecific hydrogenation
s. *9*, 74

Amines from O-alkoximes $C{:}NOR \rightarrow CHNH_2$

25.



$$\underset{\substack{\| \\ NOCH_2C_6H_5}}{CH_3C}\cdot CONHCH(CH_3)COOH \rightarrow \underset{\substack{| \\ NH_2}}{CH_3CH}CONHCH(CH_3)COOH$$

N-(α-Benzyloximinopropionyl)-DL-alanine hydrogenated 1 hr. with 10%-Pd-on-charcoal in aq. NH_3 at 4 atm. until H_2-absorption ceases after the calculated amount has been taken up → alanylalanine. Y: 90%.—In the presence of NH_3, formation of diketopiperazines is avoided. F. e. s. W. H. Hartung, D. N. Kramer, and G. P. Hager, Am. Soc. *76*, 2261 (1954).

Amines from nitroso compounds $NO \rightarrow NH_2$
s. *7*, 276

Amines from nitro compounds $NO_2 \rightarrow NH_2$
s. *9*, 569; s. a. R. A. Abramovitch and K. Schofield, Soc. *1955*, 2326

with simultaneous hydrogenolysis of benzyl ethers
s. *8*, 22

Platinum black *Pt*
s. *6*, 37

Platinum-carbon *Pt-C*
Acylamines from oximes – Selective hydrogenation $C{:}NOH \rightarrow CHNHAc$
Labeled compounds s. *7*, 46

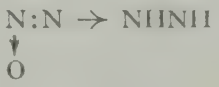
Platinum oxide *PtO_2*
Amino from oximino compounds $C{:}NOH \rightarrow CHNH_2$
s. *10*, 398

Amines from nitro compounds $NO_2 \rightarrow NH_2$
s. *6*, 37/8; *7*, 532; *8*, 563; *9*, 39; *10*, 23, 28

Aliphatic compounds
s. *7*, 47

Partial reduction
s. *8*, 23

Hydrazo from azoxy compounds
s. *9*, 40


$\underset{\substack{\downarrow\\ O}}{N}{:}N \rightarrow NHNH$

Nitrogen ↑ HN⇵N

Potassium hydroxide/alcohol *KOH*

Amines from N-nitrosamines $N{\cdot}NO \rightarrow NH$
s. *7*, 413

Lithium aluminum hydride *$LiAlH_4$*
s. *9*, 34

α-Aminoalcohols from α-diazoketones $COCHN_2 \rightarrow CH(OH)CH_2NH_2$
s. *7*, 475

Amines from azides $N_3 \rightarrow NH_2$
s. *8*, 24

Phenol/hydrobromic acid s. Hydrobromic acid/phenol *C_6H_5OH/HBr*

Urea *$CO(NH_2)_2$*

Amines from N-nitrosamines $N{\cdot}NO \rightarrow NH$
s. *7*, 48

Phenylhydrazine *$C_6H_5NHNH_2$*

Amines from azo compounds
via hydrazo compounds $N{:}NR \rightarrow NH_2$
s. *9*, 41

Hydrogen sulfide *H_2S*

Amino groups from azido groups $N_3 \rightarrow NH_2$
s. *8*, 25

Hydrosulfite *$S_2O_4^{--}$*

Amines from azides
s. *8*, 26

Hydrobromic acid/phenol *HBr/C_6H_5OH*
s. *7*, 49

Nickel *Ni*

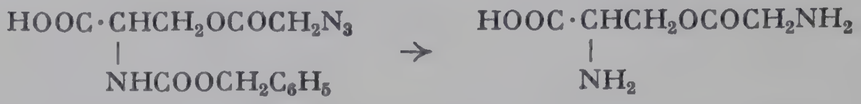
Glycosamines from glycosazides
s. *7*, 50

Palladium *Pd*

Amines from azo compounds $N{:}NR \rightarrow NH_2$
s. *8*, 27

Amines from azides $N_3 \rightarrow NH_2$
with simultaneous elimination of N-carbobenzoxy groups

26.



$$\underset{\displaystyle NHCOOCH_2C_6H_5}{HOOC\cdot \underset{|}{C}HCH_2OCOCH_2N_3}\rightarrow \underset{\displaystyle NH_2}{HOOC\cdot \underset{|}{C}HCH_2OCOCH_2NH_2}$$

A soln. of O-azidoacetyl-N-carbobenzoxy-DL-serine in HCl-methanol-water hydrogenated 3.5 hrs. with Pd-black at 3 atm. → O-glycyl-DL-serine monohydrochloride. Y: 82%. E. D. Nicolaides, R. D. Westland, and E. L. Wittle, Am. Soc. *76*, 2887 (1954); amines from azides with Pd-C s. H. Bretschneider et al., M. *84*, 1021, 1033, 1043 (1953).

Palladium-carbon *Pd-C*

Replacement of N-nitro groups by hydrogen $N\cdot NO_2 \rightarrow NH$
s. *7*, 51

Amines from azides $N_3 \rightarrow NH_2$
s. *10*, 26

Platinum oxide *PtO_2*

27. *trans*-2-Azidocyclohexanol (prepn. s. 262) hydrogenated 24-48 hrs. with PtO_2 at 3 atm. → *trans*-2-aminocyclohexanol. Y: 81%. F. e. s. C. A. VanderWerf, R. Y. Heisler, and W. E. McEwen, Am. Soc. *76*, 1231 (1954).

Sulfur ↑ HN⇅S

Sodium hydroxide *NaOH*

Cleavage of sulfonic acid amides $N\cdot SO_2R \rightarrow NH$
N-Nitramines s. *6*, 39

Sodium/liq. ammonia *Na/NH_3*

N-Detosylation
s. *9*, 42; s. a. Am. Soc. *76*, 6202 (1954); cf. J. Rudinger and H. Czurbová, Collection Czech. Chem. Communs. *19*, 386, 375 (1954)

Phenol/hydrobromic acid s. Hydrobromic acid/phenol *C_6H_5OH/HBr*

Sulfuric acid *H_2SO_4*

Amines from sulfonic acid amides
s. *8*, 450, 805

Sulfuric acid/acetic acid *H_2SO_4/CH_3COOH*
s. *8*, 28

Hydrochloric acid *HCl*
s. *3*, 22; s. a. T. L. Fletcher, M. E. Taylor, and A. W. Dahl, J. Org. Chem. *20*, 1020 (1955)

Amines from sulfamic acids $NHSO_3H \rightarrow NH_2$
s. *7*, 52

Benzisothiazole ring opening ↻
s. *8*, 33

Hydrobromic acid/phenol *HBr/C_6H_5OH*

Amines from sulfonic acid amides $N \cdot SO_2R \rightarrow NH$

s. *8*, 29

Palladium-carbon *Pd-C*

Thioethers from sulfilimines ←

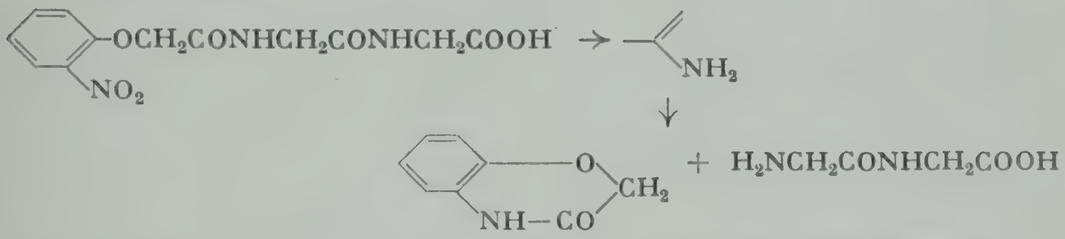
s. *8*, 374

Carbon ↑ HN⇅C

Without additional reagents *w.a.r.*

Removal of o-nitrophenoxyacetyl protective groups from peptides NAc → NH

28.



An aq. soln. of o-nitrophenoxyacetylglycylglycine and $NaHCO_3$ containing PtO_2 hydrogenated 30-40 min. until the theoretical amount of H_2 has been absorbed, and the resulting crude o-aminophenoxyacetylglycylglycine heated ca. 1 hr. with water at 100° → glycylglycine. Y: 73%. F. e. s. R. W. and A. D. Holley, Am. Soc. *74*, 3069 (1952).

Sec. amines from quaternary N-halogenammonium salts $R_3N^+ \cdot Hal, Hal^- \rightarrow R_2NH$

s. *7*, 542

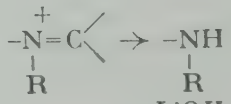
α-Aminocarboxylic acid amides from oxazolidines C

s. *6*, 347

Alkali ←

Sec. amines from azomethinium salts

s. *10*, 703

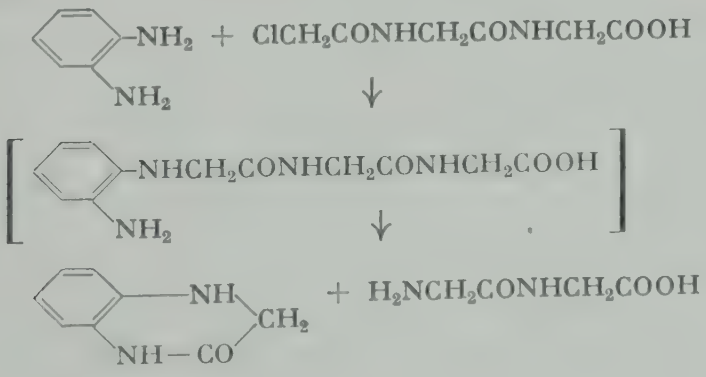


$-\overset{+}{\underset{R}{N}}=C\langle \rightarrow -\underset{R}{N}H$

Lithium hydroxide *LiOH*

Removal of N-chloroacetyl protective groups from peptides NAc → NH

29.



An aq. soln. of N-chloroacetylglycylglycine, o-phenylenediamine dihydrochloride, and LiOH heated 1 hr. on a water bath → glycylglycine. Y: 76%. F. e. s. R. W. and A. D. Holley, Am. Soc. *74*, 3069 (1952).

Sodium hydroxide *NaOH*

α-Aminocarboxylic acids from α-formamidomalonic esters
s. *6*, 127, 789

Partial N-deacylation
s. *9*, 43

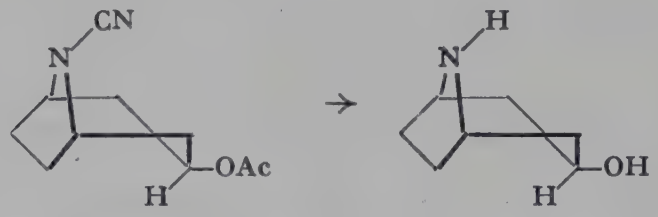
Selective hydrolysis – Blocking of amino groups
s. *9*, 44

Elimination of N-carbethoxy groups N·COOR → NH
s. *6*, 40

Stepwise degradation of peptides ←
Elimination of terminal moieties
s. *8*, 475

Amines from cyanamides N·CN → NH
with simultaneous O-deacetylation

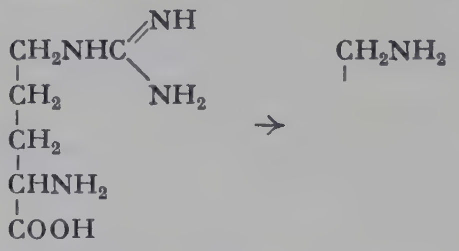
30.



A soln. of crude N-cyanonorpseudotropine acetate in aq. NaOH refluxed 7.5 hrs. → norpseudotropine. Y: 86.5%. A. Nickon and L. F. Fieser, Am. Soc. *74*, 5566 (1952).

Amines from guanidines $NHC(:NH)NH_2 \rightarrow NH_2$

31.



$$CH_2NHC(=NH)NH_2-CH_2-CH_2-CHNH_2-COOH \rightarrow CH_2NH_2-$$

L-Arginine monohydrochloride refluxed 16 hrs. in 20%-NaOH, and the product isolated as the monohydrochloride → DL-ornithine monohydrochloride. Y: 85-90%. P. B. Hamilton and R. A. Anderson, Biochem. Prep. *3*, 96 (1953).
L-Arginine monohydrochloride refluxed 2 hrs. in satd. aq. $Ba(OH)_2$, and the product isolated as the hydrochloride → L-ornithine mono-

hydrochloride. Y: 59-66%. D. E. Rivard, Biochem. Prep. *3*, 97 (1953); Am. Soc. *77*, 1260 (1955).

o-Aminocarboxylic acids ⊂
from 2,4-dioxo-1,2,3,4-tetrahydroquinazolines
s. *10*, 532

Potassium hydroxide *KOH*

Amines from acylamines NAc → NH
s. *6*, 502; *8*, 195

Alkoxylamines from alkoxyurethans RONHCOOR′ → RONH
s. *7*, 53

2-Aminoalcohols and 2-oxazolidones ←
from amines via halogenourethans
s. *9*, 45

Hydantoin ring opening ⊂
s. *8*, 30

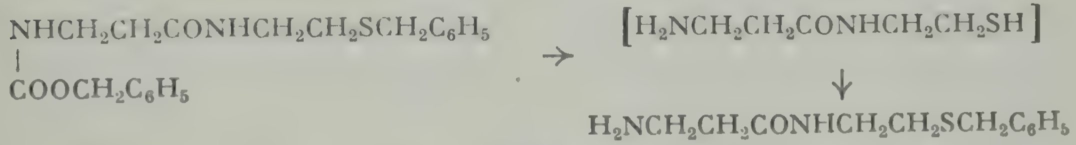
Aminophenols from benzoxazolone ring
s. *7*, 54

Sodium/liq. ammonia *Na/NH$_3$*

Amines from urethans NCOOR → NH
Cleavage of carbalkoxy derivatives of amines
s. *7*, 55; *8*, 684

N-Decarbobenzoxylation
with simultaneous formation of
mercaptans from benzylthioethers
s. *9*, 56

32.



$$\begin{array}{lcc} \mathrm{NHCH_2CH_2CONHCH_2CH_2SCH_2C_6H_5} & & [\mathrm{H_2NCH_2CH_2CONHCH_2CH_2SH}] \\ | & \rightarrow & \downarrow \\ \mathrm{COOCH_2C_6H_5} & & \mathrm{H_2NCH_2CH_2CONHCH_2CH_2SCH_2C_6H_5} \end{array}$$

with S-rebenzylation. Liq. NH$_3$ added to N-(N-carbobenzoxy-β-alanyl)-S-benzyl-β-aminoethanethiol, then Na added to the stirred mixture until a permanent blue color is obtained, cooled in a Dry Ice-alcohol bath, benzyl chloride added slowly, NH$_3$ allowed to evaporate at room temp., near the end of the evaporation NH$_4$-sulfate added, the last NH$_3$-traces removed under reduced pressure, and the product isolated as the hydrochloride → N-β-alanyl-S-benzyl-β-aminoethanethiol hydrochloride. Y: 88%. E. Walton et al., Am. Soc. *76*, 1146 (1954); s. a. J. Baddiley and A. P. Mathias, Soc. *1954*, 2803.

Sodium sulfite *Na$_2$SO$_3$*

Pyrazine ring degradation ⊂
s. *6*, 41

Ammonia *NH_3*

Amines from trifluoroacetylamines $NCOCF_3 \rightarrow NH$
s. *10*, 405

Selective deacylation $NAc \rightarrow NH$
s. *7*, 56

Amines *$R{\cdot}NH_2$*

Carboxylic acid hydrazides from 1,3,4-oxadiazol-2(3H)-ones C
s. *10*, 261

Barium hydroxide *$Ba(OH)_2$*

Selective N-decarbomethoxylation $NCOOCH_3 \rightarrow NH$
s. *8*, 31

Amines from guanidines $NHC(:NH)NH_2 \rightarrow NH_2$
s. *10*, 31

Lithium aluminum hydride *$LiAlH_4$*

Amines from acylamines $NAc \rightarrow NH$
s. *8*, 32

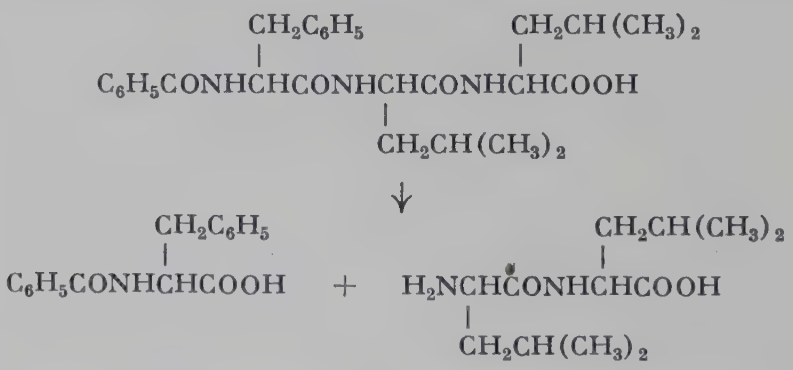
Ammonium acetate *CH_3COONH_4*

N-Deacylation
s. *9*, 46

Chymotrypsin ←

Enzymatic removal of N-protective groups from peptides ←
Removal of the benzoyl-L-phenylalanyl group

33.



$$C_6H_5CONH\overset{CH_2C_6H_5}{CH}CONH\underset{CH_2CH(CH_3)_2}{CH}CONH\overset{CH_2CH(CH_3)_2}{CH}COOH \rightarrow C_6H_5CONH\overset{CH_2C_6H_5}{CH}COOH + H_2N\underset{CH_2CH(CH_3)_2}{CH}CONH\overset{CH_2CH(CH_3)_2}{CH}COOH$$

A soln. of benzoyl-L-phenylalanyl-L-leucyl-L-leucine in aq. NaOH containing chymotrypsin allowed to stand 8 hrs. at room temp. and pH 7.3 → L-leucyl-L-leucine hydrate. Y: 80%. R. W. Holley, Am. Soc. 77, 2552 (1955).

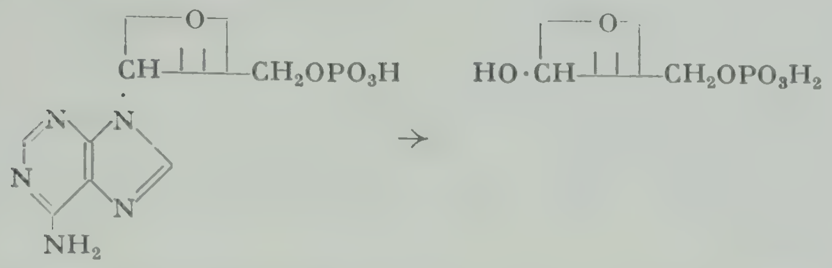
Hog kidney enzyme ←

Resolution of racemates by enzymic hydrolysis
Amines from acylamines
s. *6*, 42

Dowex-50-H⁺ resin ←

Cleavage of nucleotides ←

34.



Adenosine-5′-phosphate added with vigorous stirring at 100° to a mixture of Dowex-50-H$^+$ resin and water, the product isolated after 4 min. as the Ba-salt → Ba-ribose-5-phosphate. Y: ca. 95%. J. X. Khym, D. G Doherty, and W. E. Cohn, Am. Soc. *76*, 5523 (1954).

Formic acid $HCOOH$

Amines from isothiocyanates $N:C:S \rightarrow NH_2$
s. *6*, 43

Acetic acid CH_3COOH

2-Aminoalcohols from oxazolidines C
s. *6*, 73

Hydrazine $H_2N{\cdot}NH_2$

Prim. amines from phthalimides $\left|\begin{matrix}CO\\CO\end{matrix}\right\rangle NR \rightarrow H_2NR$
Mild hydrolysis in the cold s. *6*, 342

Oxazole ring opening C
s. *7*, 388

Phenylhydrazine $C_6H_5NHNH_2$

Prim. amines from phthalimides $\left|\begin{matrix}CO\\CO\end{matrix}\right\rangle NR \rightarrow H_2NR$
Aminocarboxylic acids s. *7*, 57

Sulfuric acid H_2SO_4

Amines from acylamines $NAc \rightarrow NH$
s. *9*, 416

Cleavage of nucleosides ←
with subsequent replacement of amino groups by hydroxyl
s. *6*, 44

Amines from cyanamides $N{\cdot}CN \rightarrow NH$
s. *6*, 45

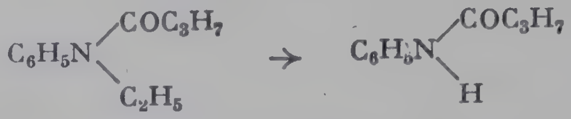
Sulfuric acid/ammonium chloride H_2SO_4/NH_4Cl

Selective N-deacylation $NAc \rightarrow NH$
s. *9*, 47

Pyridine hydrochloride *C_5H_5N,HCl*

N-Dealkylation NR → NH

35.



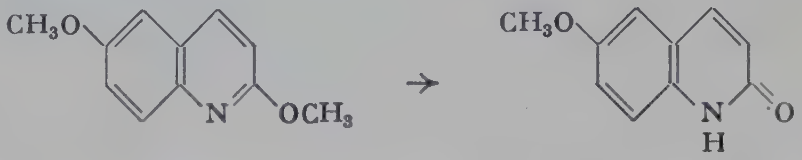
$C_6H_5N\langle^{COC_3H_7}_{C_2H_5} \rightarrow C_6H_5N\langle^{COC_3H_7}_{H}$

New method. N-Ethylbutyranilide heated 6 hrs. with 6.7 moles pyridine hydrochloride at 190-200° → butyranilide. Y: 96%. F. e. s. D. Klamann and E. Schaffer, B. *87*, 1294 (1954); also prepn. of anhydrous pyridine s. M. *84*, 925 (1953).

Hydrochloric acid *HCl*

Selective O-dealkylation ←

36.



Carbostyrils. 2,6-Dimethoxyquinoline boiled 48 hrs. with aq. 6 *N* HCl, and the solid product stirred with hot aq. 10%-NH_3 → 6-methoxycarbostyril. Y: 89%. R. R. Holmes et al., Am. Soc. *76*, 2400 (1954).

Imidazoles from isoimidazoles with hydrolysis ←
s. *9*, 420

Amines from acylamines – Selective hydrolysis NAc → NH
s. *6*, 26; *9*, 392

Aminosulfonic acid amides
from acylaminosulfonic acid amides
s. *9*, 392

Aminoalcohols from halogenoacylamines
s. *9*, 330

Amines from diacylamines $N(Ac)_2 \rightarrow NH_2$
s. *10*, 399

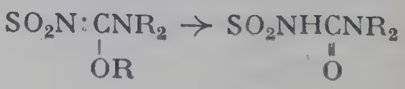
Elimination of the N-carbethoxy group N·COOR → NH
s. *6*, 465

Amines from isocyanates N:C:O → NH_2
s. *6*, 381

Amines from aminomethylolsulfites $NHCH_2OSO_2H \rightarrow NH_2$
s. *7*, 499

***α*-Aminocarboxylic acids from polypeptides** ←
s. *8*, 569

Sulfonylureas from sulfonylisoureas
s. *7*, 58



$SO_2N{:}\underset{OR}{\underset{|}{C}}NR_2 \rightarrow SO_2NH\underset{O}{\underset{\|}{C}}NR_2$

Imidazolidine ring opening C
s. *9*, 48

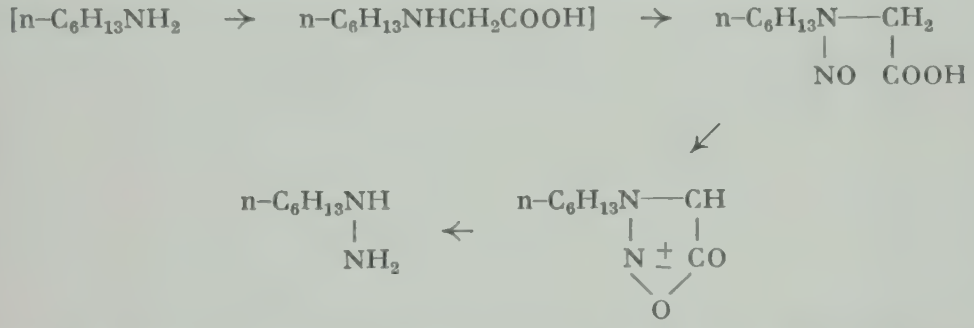
2-Aminoalcohols from 2-oxazolidones
Cleavage of ethers
s. *7*, 59

α-Aminocarboxylic acids from 2,5-oxazolidiones
s. *9*, 49

Benzisothiazole ring opening
s. *8*, 33

Monosubst. hydrazines
from α-N-nitrosaminocarboxylic acids via sydnones

37.



Crude N-nitroso-N-n-hexylglycine heated 2 hrs. with acetic anhydride on a steam bath, excess acetic anhydride removed under reduced pressure, the resulting crude N-n-hexylsydnone heated 2 hrs. with concd. HCl on a steam bath, and the product isolated as the hydrogen oxalate → crude n-hexylhydrazine hydrogen oxalate. Y: 77%.—These are the last steps of a synthesis of monosubst. hydrazines from prim. amines via the corresponding glycines and N-nitrosoglycines. The synthesis can be performed without purifying any of the intermediates. F. e. s. J. Fugger, J. M. Tien, and I. M. Hunsberger, Am. Soc. *77*, 1843 (1955).

Hydrobromic acid *HBr*

Amines from urethans NCOOR → NH
s. *9*, 50

Selective elimination of N-carbobenzoxy groups
s. *9*, 51

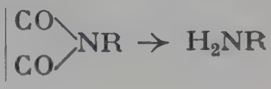
Protection of amino groups ←
Selective removal of N-protecting groups from peptides

38. The following scheme for selective cleavage of N-protecting groups is suggested: N-Carbobenzoxy with HBr in glacial acetic acid at 20°, N-carbophenoxy by catalytic hydrogenation with PtO_2 in glacial acetic acid, N-tosyl with Na in liq. NH_3, N-formyl by methanolysis, and N-phthaloyl with hydrazine or phenylhydrazine. E. s. R. A. Boissonnas and G. Preitner, Helv. *36*, 875 (1953).

Hydriodic acid *HI*

Amines from acylamines – Selective hydrolysis NAc → NH
s. *6*, 26

Prim. amines from phthalimides with simultaneous replacement of bromine by iodine
s. *8*, 625


$\left|\begin{array}{l}CO\\CO\end{array}\right\rangle NR \rightarrow H_2NR$

Potassium ferricyanide *$K_3[Fe(CN)_6]$*

N-Demethylation $NCH_3 \rightarrow NH$
s. *7*, 60

Nickel *Ni*

Sec. from tert. amines NR → NH
s. *8*, 34

Palladium *Pd*

Elimination of N-carbobenzoxy groups $NCOOCH_2C_6H_5 \rightarrow NH$
s. *10*, 26

Selective elimination from tosylcarbobenzoxypeptides
s. *7*, 61

Simultaneous cleavage of carbobenzoxy derivatives of amines and benzyl esters
Peptides s. *7*, 62

Simultaneous N-decarbobenzoxylation of amines and carboxylic acid hydrazides
s. *9*, 52

Palladium/platinum oxide s. Platinum oxide/palladium *Pd/PtO_2*

Palladium-carbon *Pd-C*

Hydrogenolysis of amines NR → NH
s. *9*, 53; s. a. R. Baltzly and P. B. Russell, Am. Soc. *76*, 5776 (1954)

Debenzylation
s. *6*, 364

Prim. amines from sec. aminoketones
s. *8*, 487

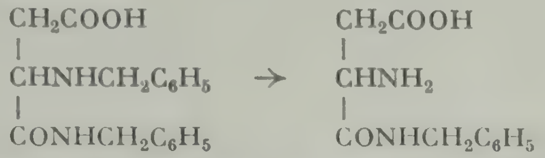
Simultaneous cleavage of carbobenzoxy derivatives of amines and benzyl esters NCOOR → NH
s. *9*, 860

Palladous oxide *PdO*

Cleavage of carbo-p-nitrobenzoxy derivatives of peptides
s. *9*, 54

Palladous chloride-carbon *$PdCl_2$-C*

Selective N-debenzylation $NCH_2C_6H_5 \rightarrow NH$

39. 

$$\begin{array}{l}CH_2COOH\\ |\\ CHNHCH_2C_6H_5\\ |\\ CONHCH_2C_6H_5\end{array} \rightarrow \begin{array}{l}CH_2COOH\\ |\\ CHNH_2\\ |\\ CONHCH_2C_6H_5\end{array}$$

30%-Pd-chloride-on-carbon added to a soln. of N,N′-dibenzyl-α-dl-asparagine in glacial acetic acid, and hydrogenated ca. 5 hrs. at 60-70° in a Parr low pressure apparatus → N′-benzyl-α-dl-asparagine. Y: 90%. F. e. s. Y. Liwschitz and A. Zilkha, Am. Soc. *76*, 3698 (1954).

Platinum oxide/palladium *PtO_2/Pd*

Simultaneous removal of protective groups
Cleavage of carbobenzoxy derivatives of amines NCOOR → NH
s. *7*, 31

Elimination

Carbon ↑ **HN ⇑ C**

Hydrochloric acid *HCl*

Oxazolidine ring opening with acyl migration ↻
O-Acyl from N-acyl
s. *8*, 35

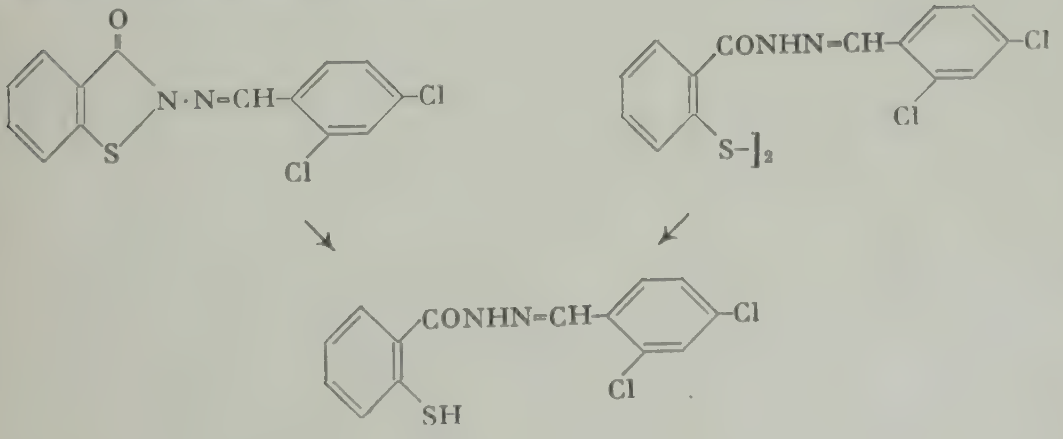
Formation of H—S Bond

Uptake

Addition to Nitrogen and Sulfur HS ⇓ NS

Hydrazine *$H_2N{\cdot}NH_2$*

Benzisothiazolone ring opening ↻
Mercaptans from disulfides

40. 

Hydrazine hydrate added at room temp. to a slurry of 1 g.

(2,4-dichlorobenzal)-2-aminobenzisothiazolone | bis-(2,4-dichlorobenzal)dithiosalicylhydrazide

in pyridine-methanol, and the product isolated after

15 sec. ↘ | ↙ 15 min.

0.9 g. (2,4-dichlorobenzal)thiosalicylhydrazide 0.8 g.

L. Katz and W. Schroeder, J. Org. Chem. *19*, 103 (1954).

Exchange

Oxygen ↑ HS⇅O

Lithium aluminum hydride $LiAlH_4$

Mercaptans from sulfonic acid anhydrides $(RSO_2)_2O \rightarrow 2\,RSH$

s. *8*, 36

Halogen ↑ HS⇅Hal

Zinc amalgam *Zn,Hg*

Mercaptans from sulfonic acid chlorides $SO_2Cl \rightarrow SH$

s. *8*, 37

Lithium aluminum hydride $LiAlH_4$

Reduction of sulfur compounds
Mercaptans from sulfonic acid chlorides $SO_2Cl \rightarrow SH$
Sym. disulfides from thiosulfonates $RSO_2SR \rightarrow RSSR$

s. *6*, 47

Stannous chloride $SnCl_2$

Mercaptans from sulfonic acid chlorides $SO_2Cl \rightarrow SH$

s. *8*, 37

Sulfur ↑ HS⇅S

Zinc/acetic acid Zn/CH_3COOH

Mercaptans from disulfides $RSSR \rightarrow 2\,RSH$

s. *8*, 38; s. a. T. Wieland et al., A. *587*, 146 (1954)

Zinc/hydrochloric acid Zn/HCl

s. *6*, 48

Lithium aluminum hydride $LiAlH_4$

s. *6*, 47

Hydrazine $H_2N{\cdot}NH_2$

s. *10*, 40

Sodium sulfide Na_2S

s. *6*, 660

Sodium hydrogen sulfide *NaHS*

s. *8*, 39

Carbon ↑ HS⇅C

Sodium hydroxide *NaOH*

Mercaptans from isothioureas $SC(:NH)NH_2 \rightarrow SH$
s. *10*, 461

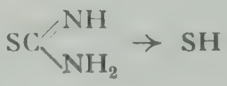
Benz-1,3-oxathiolone ring closure and opening ←
s. *9*, 55

Sodium hydroxide/alcohol

Mercaptans from thiolic acid esters $SCOR \rightarrow SH$
s. *6*, 51

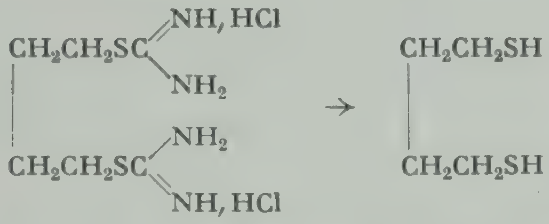
Potassium hydroxide *KOH*

Mercaptans from isothioureas



$SC(=NH)NH_2 \rightarrow SH$

41.



$CH_2CH_2SC(=NH\cdot HCl)NH_2 \ / \ CH_2CH_2SC(NH_2)=NH\cdot HCl \rightarrow CH_2CH_2SH \ / \ CH_2CH_2SH$

Dithiols. An aq. soln. of 100 g. butane-1,4-diisothiouronium dihydrochloride, stirred and treated with aq. KOH (3 molar equivalents per isothiouronium salt group, just sufficient to liberate the thiol in the free state and avoiding formation of the alkali metal mercaptide, heated and flushed with N_2 until refluxing starts, refluxing continued 4-7 hrs. until NH_3 is no longer evolved, and the product isolated in a N_2 atmosphere → butane-1,4-dithiol. Y: 88%. F. e. s. C. H. Grogan, L. M. Rice, and E. E. Reid, J. Org. Chem. *20*, 50 (1955).

Potassium hydroxide/alcohol

Mercaptans from thioethers $RSR \rightarrow RSH$
s. *10*, 475

Thiazole ring opening ⊂
s. *6*, 49

Sodium/liq. ammonia *Na/NH_3*

Mercaptans from benzyl thioethers with simultaneous N-decarbobenzoxylation $RSCH_2C_6H_5 \rightarrow RSH$
s. *9*, 56

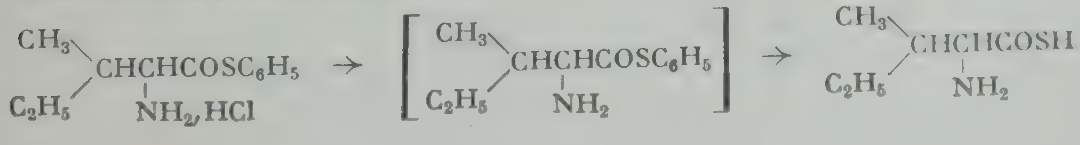
Ammonia *NH_3*

Mercaptans from xanthates $SC(:S)OR \rightarrow SH$
s. *6*, 656

Triethylamine *$(C_2H_5)_3N$*

Thiolic acids from their esters $COSR \rightarrow COSH$

42.



$(CH_3)(C_2H_5)CHCH(NH_2,HCl)COSC_6H_5 \rightarrow [(CH_3)(C_2H_5)CHCH(NH_2)COSC_6H_5] \rightarrow (CH_3)(C_2H_5)CHCH(NH_2)COSH$

Aminothiolic acids. A suspension of isoleucylthiophenol hydrochloride in abs. ether treated with triethylamine, vigorously shaken for 15 min., triethylamine hydrochloride removed by filtration, and H_2S passed in at 0° for 2 hrs. → thioisoleucine. Y: 66%. F. e. and procedure s. T. Wieland et al., B. *87*, 1093, 1099 (1954).

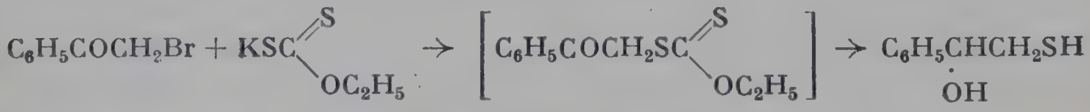
Lithium aluminum hydride *$LiAlH_4$*

Mercaptans from thiocyanates SCN → SH

s. *6*, 47; s. a. O. Hromatka and I. Kirnig, M. *85*, 235 (1954)

Mercaptans from halides via xanthates ←

43.



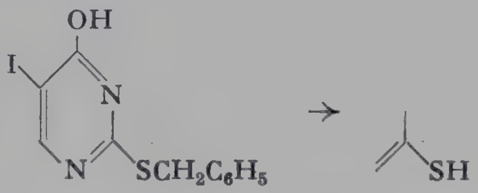
$$C_6H_5COCH_2Br + KSC(=S)OC_2H_5 \rightarrow \left[C_6H_5COCH_2SC(=S)OC_2H_5\right] \rightarrow C_6H_5CH(OH)CH_2SH$$

Hydroxymerceptans. A soln. of K-ethylxanthate in acetone added slowly below 10° to phenacyl bromide in acetone, filtered, evaporated, dried 30 min. at 60° in vacuo, then refluxed overnight with $LiAlH_4$ in ether under N_2 → 1-phenyl-2-mercaptoethanol. Y: 87%. F. e., also isolation of the intermediate xanthates, s. C. Djerassi et al., Am. Soc. *77*, 568 (1955).

Aluminum bromide *$AlBr_3$*

Mercaptans from thioethers RSR → RSH

44.



5-Iodo-2-benzylthiouracil added rapidly with stirring to a soln. of $AlBr_3$ in dry toluene, and kept 6 hrs. at 60° with continued stirring after the exothermic reaction has subsided → 5-iodo-2-thiouracil. Y: 81.6%. Scope and limitations. s. A. E. Lanzilotti, J. B. Ziegler, and A. C. Shabica, Am. Soc. *76*, 3666 (1954).

Phosphorus/iodine *P/I*

s. *6*, 50

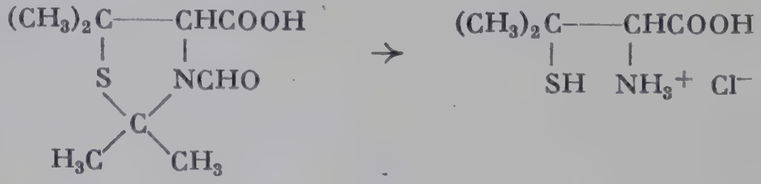
Hydrochloric acid *HCl*

Mercaptans from thiolic acid esters SCOR → SH

Deacetylation s. *6*, 51

Thiazolidine ring opening C

45.



N-Formylisopropylidene-D-penicillamine heated ca. 1 hr. in 2 *N* HCl on a steam bath until dissolved, while a CO_2-stream is passed through → D-penicillamine hydrochloride. Y: 99%. Also L-isomer s. B. E. Leach and J. H. Hunter, Biochem. Prep. *3*, 111 (1953).

Elimination

Sulfur ↑ HS ⇑ S

Hydrochloric acid *HCl*

Mercaptans from alkylthiosulfates $R{\cdot}S{\cdot}SO_3^- \rightarrow R{\cdot}SH$

s. *7*, 63; s. a. H. Z. Lecher and E. M. Hardy, J. Org. Chem. *20*, 475 (1955)

Carbon ↑ HS ⇑ C

Electrolysis ↯

Thiazoline ring opening C

s. *8*, 653

Formation of H—Rem Bond

Exchange

Halogen ↑ HRem ⇅ Hal

Sodium carbonate *Na_2CO_3*

Phosphines from chlorophosphines by disproportionation ←

s. *9*, 57

Zinc-copper *Zn-Cu*

Arsines from halogenarsines ←

46. $CF_3AsI_2 \rightarrow CF_3AsH_2$

Trifluoromethyl arsenicals. Diiodo(trifluoromethyl)arsine added portionwise with vigorous shaking to Zn coated with Cu in aq. HCl, concd. HCl added portionwise during 1 hr. after which the apparatus is flushed with N_2 for 1 hr. → trifluoromethylarsine. Y: 98%. F. reactions s. H. J. Emeléus, R. N. Haszeldine, and E. G. Walaschewski, Soc. *1953*, 1552.

Lithium aluminum hydride *$LiAlH_4$*

Silanes from halogenosilanes SiHal → SiH

s. *6*, 52

Germanes from halogenogermanes GeHal → GeH

s. *7*, 547

Remaining Elements ↑ HRem ⇅ Rem

Sodium/liq. ammonia *Na/NH_3*

Selenols from diselenides RSeSeR → 2 RSeH

s. *9*, 58

Carbon ↑ **HRem ⇅ C**

Sodium, potassium *Na,K*

Cleavage of silanes via silylpotassium ←
s. *7*, 64

Formation of H—C Bond

Uptake

Addition to Oxygen and Carbon HC ⇓ OC

Irradiation/acetic acid s. Acetic acid/irradiation ←

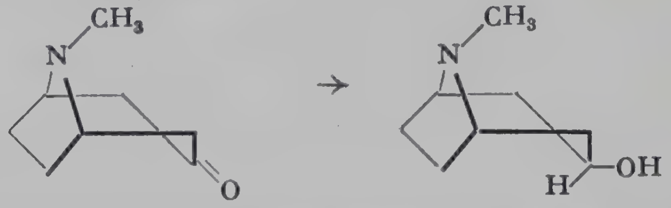
Lithium *Li*

Ring opening of heterocyclics C
s. *9*, 59

Sodium *Na*

Sec. alcohols from ketones CO → CHOH

47.



A soln. of tropinone in toluene-isobutanol added during 15 min. with vigorous stirring to Na in boiling toluene, then gently refluxed with stirring for 2 additional hrs. → pseudotropine. Y: 71%. A. Nickon and L. F. Fieser, Am. Soc. *74*, 5566 (1952); modified Bouveault-Blanc method according to V. L. Hansely, Ind. Eng. Chem. *39*, 55 (1947); s. a. K. Alder and H. A. Dortmann, B. *87*, 1905 (1954).

s. a. *7*, 101; in ether-water s. *8*, 40; s. a. J. Colonge and A. Arsac, Bl. *1954*, 445

6α- and 11α-Hydroxysteroids
Protection of carbonyl groups
by formation of ethylene ketals
s. *8*, 41

Stereoisomers
s. *7*, 65

Sodium amalgam *Na,Hg*

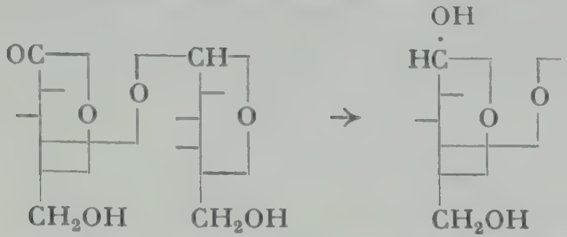
Modified procedure
s. *7*, 66

Hydroxyaldehydes from lactones ←
Carbohydrates
s. *4*, 47; in the presence of sodium hydrogen oxalate s. A. C. Neish, Can. J. Chem. *32*, 334 (1954); H. L. Frush and H. S. Isbell, J. Research Natl. Bur. Standards *51*, 307 (1954)

Sodium amalgam/sodium hydrogen oxalate *Na,Hg/HOOC·COONa*

Carbohydrates from aldonic acid lactones

48.



Na,Hg-pellets added to lactobionic lactone and ice-water buffered by Na-oxalate and oxalic acid, then stirred vigorously with ice-cooling until after ca. 2 hrs. the amalgam is spent → lactobiose. Y: 84% (by analysis). Also 1-C^{14} labeled s. H. L. Frush and H. S. Isbell, J. Research Natl. Bur. Standards *50*, 133 (1953).

Sodium hydroxide *NaOH*

Prim. alcohols and carboxylic acids from aldehydes 2 CHO → CH_2OH + COOH

Cannizzaro reaction with aliphatic aldehydes

s. 7, 67

Potassium hydroxide/formaldehyde *KOH/CH_2O*

Prim. alcohols from aldehydes CHO → CH_2OH

Cannizzaro reaction

s. 8, 42

Combined Mannich-Cannizzaro reaction

s. 7, 807

Lithium/liq. ammonia/alcohol *$Li/NH_3/ROH$*

Sec. alcohols from ethyleneketones via ketones ←

11α-Hydroxysteroids

s. 8, 43; 11α-hydroxy- from 11-ketosteroids s. a. W. S. Allen et al., Am. Soc. 77, 4784 (1955)

Lithium iodide/sodium boron hydride *$LiI/NaBH_4$*

s. Sodium boron hydride/lithium iodide

Calcium oxide/formaldehyde *CaO/CH_2O*

Sec. alcohols from ketones CO → CHOH

Cannizzaro reaction with simultaneous hydroxymethylation

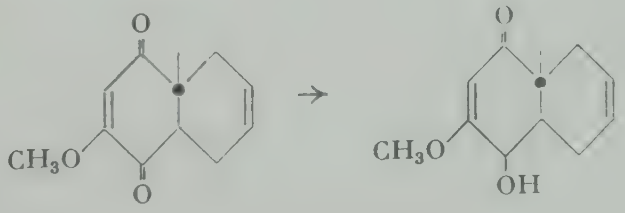
s. 7, 698

Zinc/acetic acid *Zn/CH_3COOH*

Sec. alcohols from ketones

s. 8, 99

49.



Stereospecific reduction. Zn-dust added at 20-25° during 15 min. to a soln. of d,l-*trans*-1,4-diketo-2-methoxy-10-methyl-$\Delta^{2,6}$-hexahydronaphthalene in acetic acid-water, and stirred vigorously at 20-25° for 5 hrs. → d,l-*trans*-1-hydroxy-4-keto-2-methoxy-10-methyl-$\Delta^{2,6}$-hexahydronaphthalene (startg. m. f. 123). Y: 72-90%. A. J. Speziale, J. A. Stephens, and Q. E. Thompson, Am. Soc. *76*, 5011 (1954).

Zinc, copper/alkali hydroxide *Zn,Cu*

Carboxylic acids from lactones C

s. *7*, 68

Zinc amalgam *Zn,Hg*

Carboxylactones from 1,1-dilactones

s. *7*, 103

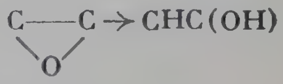
Aluminum amalgam *Al,Hg*

Prim. alcohols from aldehydes CHO → CH_2OH

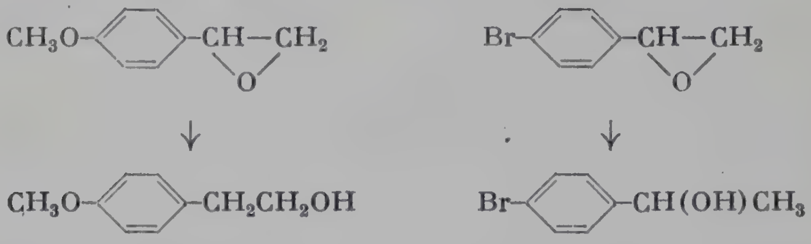
s. *7*, 133

Lithium boron hydride *$LiBH_4$*

Alcohols from oxido compounds
Direction of ring opening



50.



p-Methoxystyrene oxide	p-Bromostyrene oxide
reduced with $LiBH_4$ in ether → mixture of	
95% 2-(4-methoxyphenyl)ethanol and 5% 1-(4-methoxyphenyl)ethanol. Total Y: 70%.	84% 1-(4-bromophenyl)ethanol and 16% 2-(4-bromophenyl)-ethanol. Total Y: 66%.

F. e. and discussion s. R. Fuchs and C. A. VanderWerf, Am. Soc. *76*, 1631 (1954).

Oxido compounds from α-bromoketones via bromohydrins CO → CHOH

s. *9*, 60

Lactones from ketocarboxylic acids, nitroalcohols from nitroketones, ←

and other reactions s. *6*, 53

Sodium boron hydride/lithium iodide *$NaBH_4$/LiI*

Diols from ketocarboxylic acid esters ←

s. *9*, 876

Sodium boron hydride $NaBH_4$

Alcohols from oxo compounds CO → CHOH

s. *9*, 61; s. a. A. C. Cope and R. D. Smith, Am. Soc. *77*, 4596 (1955)

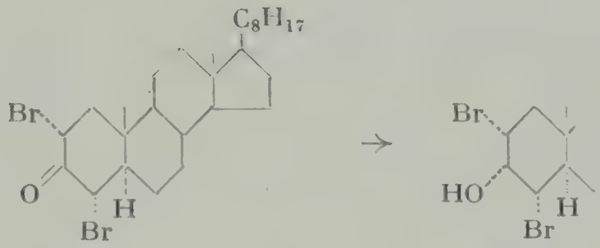
Nitroalcohols
s. *9*, 62

Special cases—
Inverse addition method
s. *9*, 63

Sec. alcohols from ketones

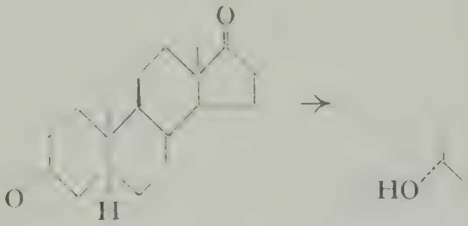
s. *10*, 67; aminosteroids s. R. A. Micheli and C. K. Bradsher, Am. Soc. *77*, 4788 (1955)

51.



Stereospecific reduction. A suspension of 1.0 g. 2α.4α-dibromocholestanone in ethanol stirred 12 hrs. at room temp. with $NaBH_4$ → 0.64 g. 2α.4α-dibromocholestan-3α-ol.—While $NaBH_4$-reduction of cholestanone leads predominantly to cholestan-3β-ol, the introduction of two α-oriented, adjacent, bulky substituents results in a reversal of the stereochemical course of this reduction. J. J. Beereboom and C. Djerassi, J. Org. Chem. *19*, 1196 (1954); reduction of steroid-7-keto groups s. E. H. Mosbach, W. Meyer, and F. E. Kendall, Am. Soc. *76*, 5799 (1954).

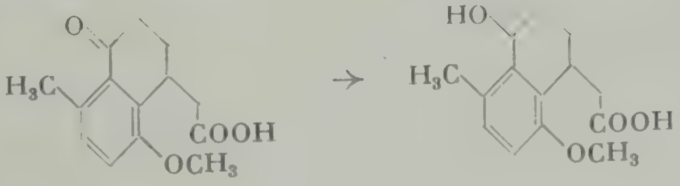
52.



Partial reduction of steroid keto groups. A soln. of etiocholane-3,17-dione in methanol added to a soln. of $NaBH_4$ in methanol-water, and the product isolated after 20 min. → 3α-hydroxyetiocholane-17-one (Y: 69%) and the 3β-hydroxy analog (Y: 17%). E. Elisberg, H. Vanderhaeghe, and T. F. Gallagher, Am. Soc. *74*, 2814 (1952); s. a. *8*, 44.

Hydroxycarboxylic acids from ketocarboxylic acids

53.

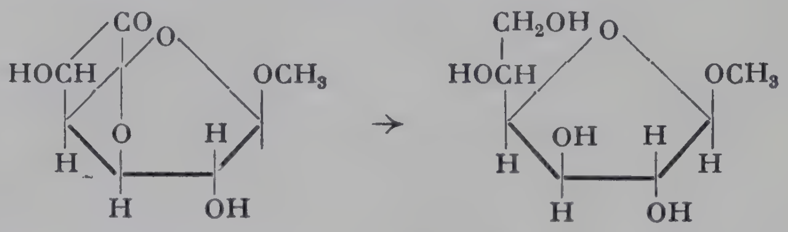


A soln. of 4-keto-5-methyl-8-methoxy-1,2,3,4-tetrahydro-1-naphthylacetic acid (prepn. s. 131) in a slight excess of aq. NaOH (just basic to phenolphthalein) treated with $NaBH_4$, and heated 1 hr. at 60-70° → 4-hydroxy-5-methyl-8-methoxy-1,2,3,4-tetrahydro-1-naphthylacetic acid. Y: 89%. A. S. Dreiding and A. J. Tomasewski, Am. Soc. *76*, 540 (1954).

$NaBH_4$ as reducing agent in the sugar series
Carbohydrates from aldonic acid lactones C
s. *8*, 45

Carbohydrates from uronic acid lactones
D-Glucofuranosides from D-glucofururonosides

54.

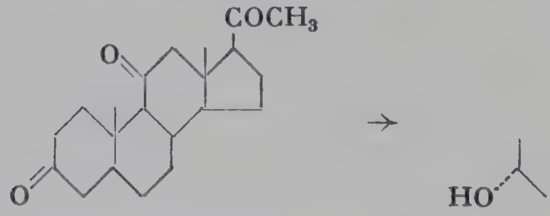


Aq. methyl β-D-glucofururonoside added during 10 min. to a stirred aq. soln. of $NaBH_4$ whereby a maximum temp. of 50° is reached, allowed to stand 10 min. at 40-45°, then excess reducing agent quenched with a few drops of dil. H_2SO_4 → methyl β-D-glucofuranoside. Y: 71%. F. e. s. D. D. Phillips, Am. Soc. *76*, 3598 (1954).

Sodium boron hydride/pyridine *$NaBH_4/C_5H_5N$*

Sec. alcohols from ketones CO → CHOH
Preferential reduction of steroid 3-keto groups

55.



A soln. of pregnane-3,11,20-trione and $NaBH_4$ in pyridine allowed to stand 7 hrs. at room temp. → pregnan-3α-ol-11,20-dione. Y: 82%; conversion 53%. F. e. s. O. Mancera et al., Am. Soc. *75*, 1286 (1953); s. a. A. J. Lemin and C. Djerassi, Am. Soc. *76*, 5672 (1954).

Lithium aluminum hydride *$LiAlH_4$*

Prim. alcohols from aldehydes CHO → CH_2OH
Amino-prim-alcohols s. *7*, 69

Sec. alcohols from ketones CO → CHOH
s. *6*, 54; *8*, 428; *9*, 65, 109, 352, 951

Stereoisomeric steroids
s. *6*, 55; from Δ^{16}-20-ketosteroids s. E. L. Shapiro, D. Gould, and E. B. Hershberg, Am. Soc. *77*, 2912 (1955)

Stereochemistry of isosteroids
s. *9*, 64

Asym. reduction
s. *7*, 70

Sec. ethylenealcohols from ethyleneketones
s. *6*, 56

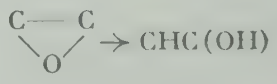
Selective reduction of cyclic unsatd. ketones
2-Ethylenealcohols from α,β-ethyleneketones
s. *10*, 90

Halogenhydrins from halogenoketones
s. *8*, 46

Hydrochalcols from chalcones C:C·CO → CH·CH·CHOH
s. *8*, 67

Hydroxymercaptans ←
s. *10*, 43

Alcohols from oxido compounds
s. *9*, 66



Optically active compounds
s. *7*, 579

with simultaneous formation of hydrocarbons and alcohols from p-toluenesulfonic acid esters
s. *8*, 90

Stereochemistry of LiAlH$_4$-reductions ←
s. *7*, 71

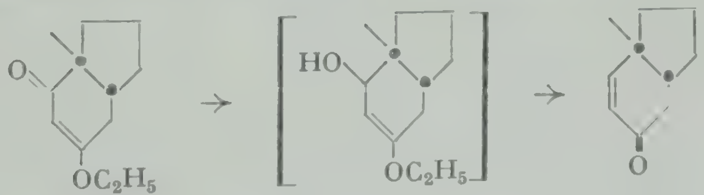
Enols from α,β-ethyleneketones ←
s. *7*, 72

Glycols from α-acoxyketones C(OAc)CO → C(OH)CH(OH)
s. *9*, 227; s. a. H. E. Zaugg, Am. Soc. *76*, 5818 (1954)

Glycols from α-diketones COCO → CH(OH)CH(OH)
s. *6*, 57

α,β-Ethyleneketones from 3-keto-1,2-en-1-olethers ←

56.



cis-5-Ethoxy-8-methyl-5-hydrinden-7-one added dropwise during 10 min. to LiAlH$_4$ in ether, stirred 0.5 hr., poured into ice and acidified

→ *cis*-8-methyl-6-hydrinden-5-one. Y: 89%.—The intermediate carbinol gives the endproduct when washed with cold, dil. acid. H. Conroy, Am. Soc. *74*, 3046 (1952).

γ-Hydroxyketones from α,β-ethylene-γ-diketones ←
1,4-Diols from γ-diketones
s. *6*, 58

Dihydroquinols from quinones ←
s. *6*, 59

Diols from lactones ⊂
s. *6*, 60; s. a. W. Schrecker and J. L. Hartwell, Am. Soc. *77*, 432 (1955)

Hydroxyaldehydes from lactones
s. *9*, 67

Diols from aldehydocarboxylic acid esters ←
s. *7*, 104

1,3-Diols $COCH_2COOR \rightarrow CH(OH)CH_2CH_2OH$
from β-ketocarboxylic acid esters
s. *8*, 93

Diols from alkoxylactones ⊂
s. *6*, 61

Partial reduction of lactams
s. *9*, 842

α-Aminoalcohols
 from α-diazoketones
 s. *7*, 475
 from acylcyanides
 s. *8*, 58

$$\begin{tikzcd}[row sep=small] COCHN_2 \arrow[dr] & \\ & CH(OH)CH_2NH_2 \\ COCN \arrow[ur] & \end{tikzcd}$$

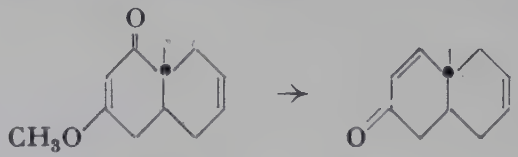
α,β-Ethylenealdehydes from α-alkoxymethyleneketones ←
s. *7*, 118

3,1-Benzoxazine ring opening ⊂
s. *9*, 68

Lithium aluminum hydride/aluminum chloride $LiAlH_4/AlCl_3$
Nitroalcohols from nitroaldehydes $CHO \rightarrow CH_2OH$
s. *10*, 62

Lithium aluminum hydride/sulfuric acid $LiAlH_4/H_2SO_4$
α,β-Ethyleneketones from 3-keto-1,2-en-1-olethers ←

57.



A soln. of (−)-*trans*-4-keto-2-methoxy-10-methyl-$\Delta^{2,6}$-hexahydronaphthalene (prepn. s. 81) in anhydrous ether added during 28 min. under N_2 to a soln. of $LiAlH_4$ in the same solvent, stirred 1.5 hrs., the crude product mixed with aq. H_2SO_4 and heated 2.5 hrs. at 95-103° with vigorous agitation → (–)-*trans*-2-keto-10-methyl-$\Delta^{3,6}$-hexahydronaphthalene. Y: over 90%. Also enantiomorph and racemate s. A. J. Speziale, J. A. Stephens, and Q. E. Thompson, Am. Soc. *76*, 5011 (1954).

Lithium aluminum hydride/hydrochloric acid *$LiAlH_4/HCl$*

Partial reductive ring opening of O-heterocyclics ↻
Furostane from spirostane ring
s. *9*, 69

Lithium aluminum deuteride *$LiAlD_4$*

Sec. alcohols from ketones CO → CDOH
Deutero compounds s. *7*, 73

Reductions with
Sodium trimethoxyboron hydride *$NaBH(OCH_3)_3$*

Alcohols from oxo compounds CO → CHOH
s. *9*, 70

Boron alkoxide *$B(OR)_3$*
s. *8*, 47

Aluminum alkoxide *$Al(OR)_3$*

Meerwein-Ponndorf-Verley reduction

Prim. alcohols from aldehydes CHO → CH_2OH
s. *6*, 62; nitro-prim-alcohols s. *7*, 74

Sec. alcohols from ketones CO → CHOH
s. *6*, 63; *7*, 891

from ketones difficult to reduce
s. *6*, 65

Stereoisomeric cyclic alcohols from cyclic ketones
s. *6*, 66

Nitroalcohols
s. *9*, 62

Hydroxysulfones from ketosulfones
s. *8*, 48

Lactols from diketones ○
s. *7*, 332

Modifications of the CO → CHOH
Meerwein-Ponndorf-Verley reduction
s. *6*, 64; *8*, 49

Aluminum alkoxide/nickel *$Al(OR)_3/Ni$*

Prim. ethylenealcohols from ethylenealdehydes CHO → CH_2OH
s. *8*, 50

Aluminum chloride/lithium aluminum hydride *$AlCl_3/LiAlH_4$*
s. Lithium aluminum hydride/aluminum chloride

Yeast ←
Biochemical reduction CO → CHOH
Partial reduction of steroid keto groups
s. *8*, 51

Acetic acid/irradiation ←
Sec. alcohols from ketones by photoreduction
s. *9*, 731

Phosphorus/iodine *P/I*
Carboxylic acids C
from phthalides
s. *9*, 366

Phosphorus/hydriodic acid *P/HI*
from alkylidenephthalides
s. *9*, 71

Copper chromite $CuCr_2O_4$
Alcohols from oxo compounds CO → CHOH
s. *6*, 108

Prim. alcohols from aldehydes CHO → CH_2OH
s. *6*, 107

Barium copper chromite $(Ba,Cu)Cr_2O_4$
s. *6*, 67 CO → CHOH

Nickel *Ni*
Prim. alcohols from aldehydes CHO → CH_2OH
s. *6*, 68; s. a. E. Kelecsenyi-Dumesnil, Bl. *1955*, 815

Aldonic acids from uronic acids
s. *8*, 52

Polyalcohols from carbohydrates
s. *9*, 72

Sec. alcohols from ketones CO → CHOH
s. *6*, 69; *9*, 352

Cyclic sec. alcohols from cyclic ketones
Elimination of the induction period
s. *6*, 70

Partial reduction of steroid keto groups
s. *9*, 73

Hydroxycarboxylic acid esters from ketocarboxylic acid esters
s. *7*, 75

β-Hydroxycarboxylic acid esters
s. *10*, 244

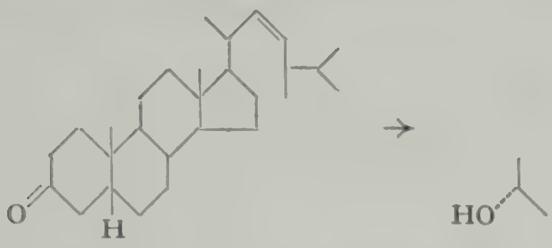
cis-trans-Isomers
s. *9*, 76

γ-Hydroxypiperidines from γ-pyridones
s. *6*, 90

Nickel/potassium hydroxide/alcohol *Ni/KOH/ROH*

Sec. ethylenealcohols from ethyleneketones

58.

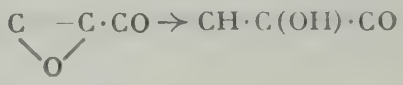


Raney-Ni sludge added to a soln. of KOH in ethanol, shaken in H_2 until the catalyst is satd., 5β-ergost-22-en-3-one then added and the reduction continued until absorption is complete → 5β-ergost-22-en-3α-ol. Y: 90%. A. F. Daglish, J. Green, and V. D. Poole, Soc. *1954*, 2627.

Nickel/aluminum alkoxide s. Aluminum alkoxide/nickel *Ni/Al(OR)₃*

Nickel/palladium *Ni/Pd*

α-Hydroxyketones from α,β-oxidoketones



$C\overset{}{—}C\cdot CO \rightarrow CH\cdot C(OH)\cdot CO$ (O bridging C—C)

s. *6*, 71

Palladium/sulfuric acid or sodium hydroxide *Pd/H₂SO₄ or Pd/NaOH*

Sec. alcohols from ketones CO → CHOH
Conditioning of catalysts
s. *6*, 72

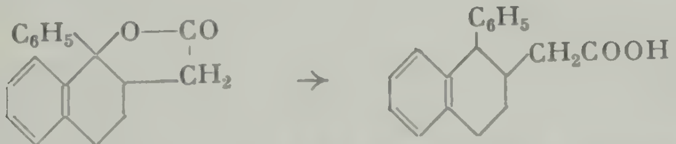
Palladium-carbon *Pd-C*

α-Aminoalcohols from α-isonitrosoketones $COC{:}NOH \rightarrow CH(OH)CHNH_2$
Stereospecific hydrogenation
s. *9*, 74

Palladous oxide *PdO*

Carboxylic acids from lactones

59.



A soln. of 1-phenyl-1-hydroxy-1,2,3,4-tetrahydro-2-naphthylacetic acid lactone in glacial acetic acid hydrogenated with prehydrogenated PdO for 6 hrs. with gentle heating during the last 3 hrs. → 1-phenyl-1,2,3,4-tetrahydronaphthyl-2-acetic acid. Y: 96%. H. Dannenberg and S. Läufer, B. *87*, 733 (1954).

Platinum oxide *PtO₂*

Sec. alcohols from ketones CO → CHOH
s. 8, 81

Glycols from acyloins $\mathrm{COCH(OH) \rightarrow CH(OH)CH(OH)}$
s. *9*, 75

α-Aminoalcohols from α-isonitrosoketones $\mathrm{COC{:}NOH \rightarrow CH(OH)CHNH_2}$
s. *6*, 79

Platinum oxide/pyridine PtO_2/C_5H_5N

Degradation of hydroxyketones to ketones via glycols

Partial reduction of steroid keto groups $\mathrm{CO \rightarrow CHOH}$
s. *8*, 53

Platinum oxide/acetic acid PtO_2/CH_3COOH

Sec. alcohols from ketones
s. *2*, 67; tropins s. J. Kebrle and P. Karrer, Helv. *37*, 484 (1954)

Hydroxycarboxylic acid esters from ketocarboxylic acid esters
cis-trans-Isomers s. *9*, 76

Via intermediates *v.i.*

Sec. alcohols from ketones
s. *7*, 679

Addition to Nitrogen and Carbon HC ⇓ NC

Electrolysis ↯

Reductive ring opening ⊂
s. *7*, 100

Medium N-heterocyclics from N-condensed rings
s. *9*, 77

Sodium *Na*

Reduction of N-heterocyclics ←
s. *8*, 86

Sodium amalgam *Na,Hg*

Thiosemicarbazides from thiosemicarbazones $\mathrm{CH{:}N{\cdot}NHCSNH_2 \rightarrow CH_2NHNHCSNH_2}$
s. *7*, 76

Opening of N-heterocyclic rings ⊂

Emde degradation
s. *8*, 54

Sodium/liq. ammonia Na/NH_3

Thiosemicarbazides from thiosemicarbazones $\mathrm{CH{:}N{\cdot}NHCSNH_2 \rightarrow CH_2NHNHCSNH}$
s. *9*, 78

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Zinc — *Zn*

α-Aminocarboxylic acids from α-ketocarboxylic acid hydrazones — $C{:}N \cdot NHR \rightarrow CHNH_2$
s. *7*, 77

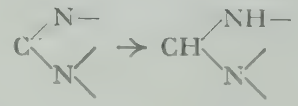
Reductive piperidone ring opening — C
s. *9*, 79

Zinc/cupric sulfate — *Zn/CuSO₄*

1,2,3,4-Tetrahydro- from 3,4-dihydro-quinolines — $C{:}N \rightarrow CHNH$
s. *8*, 55

Aluminum amalgam — *Al,Hg*

1,1-Diamines from amidines
s. *6*, 237



Sodium boron hydride — *NaBH₄*

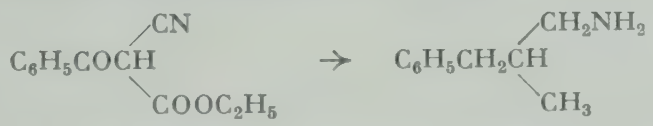
Tert. amines from quaternary ammonium salts — ←
s. *8*, 56

Lithium aluminum hydride — *LiAlH₄*

2-Ethyleneamines from α,β-ethylenenitriles — $CN \rightarrow CH_2NH_2$
s. *8*, 57

Amines from cyanoketocarboxylic acid esters — ←

60.



$$C_6H_5COCH(CN)(COOC_2H_5) \rightarrow C_6H_5CH_2CH(CH_2NH_2)(CH_3)$$

The reduction of keto and ester groups of certain compounds may proceed to the formation of methyl and methylene groups rather than stop at the alcohol stage. From nitriles, sec. amines may be obtained as by-products.—E: An ethereal soln. of ethyl benzoyl-α-cyanoacetate added dropwise with stirring during 0.5 hr. to a soln. of $LiAlH_4$ in ether, and stirring continued 4 hrs. with refluxing → 2-methyl-3-phenylpropylamine. Y: 64%. F. reductions of subst. ethyl cyanoacetates s. A. Dornow and K. J. Fust, B. *87*, 985 (1954).

2-Aminoalcohols from acylcyanides — $COCN \rightarrow CH(OH)CH_2NH_2$
s. *8*, 58; s. a. A. Dornow and H. Theidel, B. *88*, 1267 (1955)

2-Aminoalcohols from cyanohydrin acetates via oxazolidines — $CN \rightarrow CH_2NH_2$
s. *6*, 73

Aminoacetamidines from cyanoformamidines — ←
Labeled compounds s. *6*, 74

Selective ring hydrogenation of N-heterocyclics — $C{:}N \rightarrow CHNH$
s. *6*, 75

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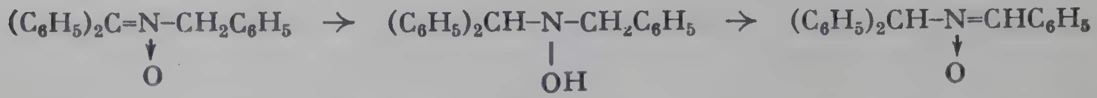
Reduction of N- and O-alkoximes ←
Hydroxylamines from nitrones
and reverse reaction

61. 

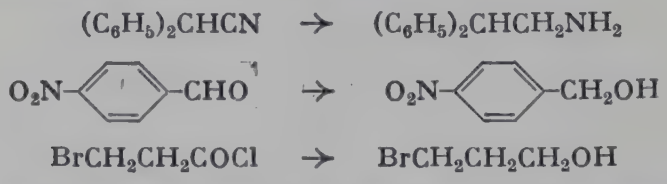
$$(C_6H_5)_2C{=}\underset{\substack{\downarrow\\ O}}{N}-CH_2C_6H_5 \rightarrow (C_6H_5)_2CH-\underset{\substack{|\\ OH}}{N}-CH_2C_6H_5 \rightarrow (C_6H_5)_2CH-\underset{\substack{\downarrow\\ O}}{N}{=}CHC_6H_5$$

A soln. of N-benzylbenzophenone oxime in benzene-ether refluxed 2 hrs. with $LiAlH_4$ → N-benzyl-N-benzhydrylhydroxylamine (Y: 90%) refluxed 4 hrs. with HgO in chloroform → N-benzhydrylbenzaldoxime (Y: 90%). F. reductions, also of alkoximes (cf. 25), and reoxidation of the hydroxylamines to the nitrones, s. O. Exner, Coll. Czech. Chem. Communs. *20*, 202 (1955).

Reductive dianthranilide ring opening
s. *9*, 81

Reductions with
Lithium aluminum hydride/aluminum chloride *$LiAlH_4/AlCl_3$*

Amines from nitriles ←
Nitroalcohols from nitroaldehydes
Halogenhydrins
from halogenocarboxylic acid chlorides

62. 

$$(C_6H_5)_2CHCN \rightarrow (C_6H_5)_2CHCH_2NH_2$$

$$BrCH_2CH_2COCl \rightarrow BrCH_2CH_2CH_2OH$$

The formation of amines from nitriles as well as the selective reduction of ar. nitroaldehydes and bromoacid chlorides can be improved by using a mixture of $LiAlH_4$ with a Lewis acid, $AlCl_3$.—E: A soln. of $AlCl_3$ in ether added rapidly to a soln. of $LiAlH_4$ in ether, after 5 min. a soln. of diphenylacetonitrile in ether added dropwise with vigorous stirring, and the product isolated 1 hr. after the addition → 2,2-diphenylethylamine. Y: 91%.—Similarly: p-Nitrobenzaldehyde → p-nitrobenzyl alcohol. Y: 75%.—3-Bromopropionyl chloride → 3-bromo-1-propanol. Y: 77%. F. e. s. R. F. Nystrom, Am. Soc. *77*, 2544 (1955).

Stannous chloride *$SnCl_2$*

Amines from nitriles – Stephen reduction $CN \rightarrow CH_2NH_2$
s. *8*, 59

Hydrosulfite *$S_2O_4^{--}$*

Aminophosphoric acids from ←
inner quaternary ammonium phosphates
s. *9*, 82

Iron *Fe*

1,2-Dihydro-N-heterocyclics from cyclic ammonium salts with simultaneous formation of amines from nitro compounds ←
s. *7*, 78

Cobalt *Co*

Amines from nitriles CN → CH_2NH_2
s. *6*, 76; ethyleneamines s. *7*, 79

Nickel-cobalt-kieselguhr *Ni-Co-SiO_2*
s. *7*, 80

Nickel *Ni*

Amines from hydrazones C:N·NH_2 → $CHNH_2$
s. *9*, 444

Amines from nitriles CN → CH_2NH_2
s. *9*, 270; *10*, 275

with simultaneous formation of prim. amines from phthalimides
s. *8*, 60

Amines from α,β-ethylenenitriles
s. *8*, 795

1,2,3,4-Tetrahydro- from 3,4-dihydro-isoquinolines C:N → CHNH
s. *9*, 84

Amines from cyclic imines C
s. *6*, 77

Nickel/potassium hydroxide *Ni/KOH*

Amines from nitriles CN → CH_2NH_2
s. *6*, 78

Palladium-carbon *Pd-C*

Sec. amines from azomethines C:N → CHNH
s. *8*, 61

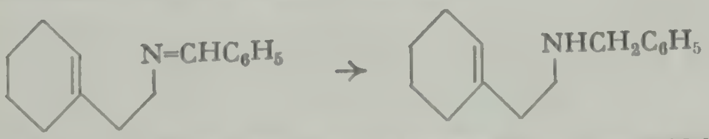
Indolines from pseudoindoles
s. *9*, 83

1,2,3,4-Tetrahydro- from 3,4-dihydro-isoquinolines
s. *9*, 84

Palladium-carbon/ammonia *Pd-C/NH_3*

Selective hydrogenation of azomethines

63.



Pd-carbon and concd. NH_3-soln. added to an alc. soln. of N-benzylidenecyclohexenylethylamine, and hydrogenated ca. 6 hrs. until the theoretical amount of H_2 has been absorbed → N-benzylcyclohexenylethylamine. Y: almost 100%. R. Grewe et al., A. *581*, 85 (1953).

Palladium-carbon/sulfuric acid *$Pd\text{-}C/H_2SO_4$*

Amines from cyanocarbonates $CN \rightarrow CH_2NH_2$

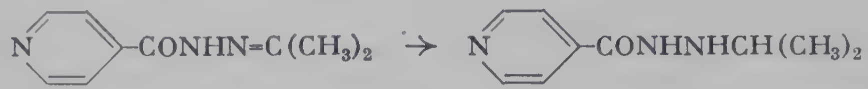
Directing the hydrogenation by acids

s. *6*, 111

Platinum oxide *PtO_2*

Hydrazines from hydrazones $C{:}N \rightarrow CHNH$

64.



Acetone isonicotinylhydrazone in abs. ethanol hydrogenated with PtO_2 at 60° and 50 lb. → 1-isonicotinyl-2-isopropylhydrazine. Y: 55%. F. e., also with a mixture of the components of the startg. m., s. H. L. Yale et al., Am. Soc. *75*, 1933 (1953).

Amines from nitriles $CN \rightarrow CH_2NH_2$

s. *7*, 81

α-Aminoalcohols from α-isonitrosoketones $C({:}NOH)CO \rightarrow CH(NH_2)CHOH$

s. *6*, 79

Ring hydrogenation ←

s. *7*, 28

1,2,3,4-Tetrahydro- from 3,4-dihydro-isoquinolines

s. *9*, 84

Tert. amines from quaternary ammonium salts

s. *9*, 949

1,2-Dihydro-N-heterocyclics from cyclic ammonium salts

s. *7*, 78

Opening of N-heterocyclic rings C

Emde degradation

s. *8*, 54

Platinum oxide/hydrochloric acid *PtO_2/HCl*

α-Aminoalcohols from cyanohydrins $C(OH)CN \rightarrow C(OH)CH_2NH_2$

s. *6*, 80

Addition to Sulfur and Carbon $HC \Downarrow SC$

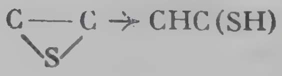
Sodium/liq. ammonia *Na/NH_3*

Reductive thiazolidine ring opening C

s. *6*, 81

Lithium aluminum hydride *$LiAlH_4$*

Mercaptans from ethylenesulfides



s. *9*, 85

Addition to Carbon

HC ⇓ CC

Without additional reagents *w.a.r.*

Carboxy-alkoxylactones from enolether-carboxylic acid anhydrides ←
s. *8*, 62

Electrolysis ↯

Partial hydrogenation C:C → CHCH

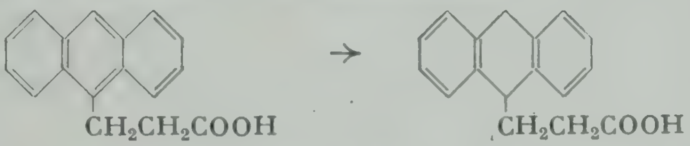
of dienes to ethylene derivatives
s. *6*, 82

of isocyclics
s. *8*, 63

Sodium *Na*

9,10-Dihydroanthracenes from anthracenes ←

65.



Na added in small pieces during 5 hrs. to a refluxing soln. of crude β-(9-anthranyl)propionic acid (prepn. s. 537) in n-amyl alcohol → β-(9,10-dihydro-9-anthranyl)propionic acid. Y: 86%. G. H. Daub and W. C. Doyle, Am. Soc. *74*, 4449 (1952).

Cyclic ketones from phenolethers ←
s. *6*, 83

Selective hydrogenation of N-heterocyclic rings ←
s. *8*, 64; to *4*, 66 s. O. Neunhoeffer and H. Ulrich, B. *88*, 1123 (1955)

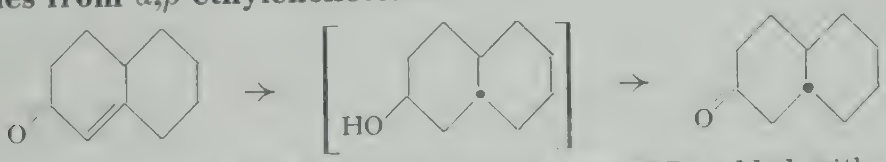
Lithium/liq. ammonia *Li/NH₃*

Ketones from ethyleneketones C:C → CHCH
Stereospecific reduction
s. *8*, 43; s. a. A. J. Lemin and C. Djerassi, Am. Soc. *76*, 5672 (1954)

Lithium/liq. ammonia—chromic acid *Li/NH₃—CrO₃*

Ketones from α,β-ethyleneketones

66.



trans-Condensed rings. 250%-excess small pieces of Li added with vigorous stirring during 3 min. to $\Delta^{1,9}$-2-octalone in liq. NH_3-ether under N_2, stirring continued for 10 min. after the initial vigorous NH_3-evolution has ceased, then excess NH_4-chloride added cautiously during 30 min., and the crude decalol oxidized with CrO_3 in acetic acid-water → 90%-*trans*-2-decalone. Y: 65-66%. E. E. van Tamelen and W. C. Proost, Jr., Am. Soc. *76*, 3632 (1954).

Lithium/liq. ammonia/alcohol $Li/NH_3/C_2H_5OH$

Partial selective hydrogenation
of carbon-carbon double bonds
s. *10*, 78

Cyclohexenones from phenolethers ←
Improved Birch reduction
Partial hydrogenation of isocyclics
Ketones from enolethers, also with migration
of a carbon-carbon double bond

s. *9*, 86; with simultaneous reduction of esters to alcohols s. A. Sandoval et al., Am. Soc. *77*, 148 (1955); partial hydrogenation of isocyclics s. a. W. Hückel and H. Schlee, B. *88*, 346 (1955)

Sodium/liq. ammonia Na/NH_3

Hydrocarbons from α,β-ethylenealcohols $C{:}C{\cdot}C(OH) \rightarrow CH{:}CH{\cdot}CH$
s. *6*, 138

Ethylene from acetylene derivatives $C\vdots C \rightarrow CH{:}CH$
cis-trans-Isomers s. *8*, 71

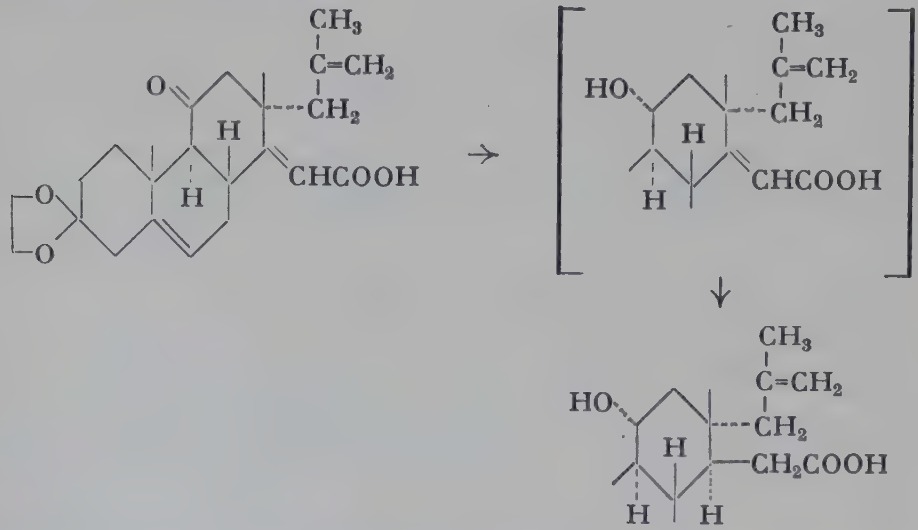
Sodium/liq. ammonia/alcohol $Na/NH_3/C_2H_5OH$

Cyclohexenones from phenolethers ←
Birch reduction
Partial hydrogenation
of carbon-carbon double bonds and isocyclics
s. *9*, 87

Potassium/liq. ammonia/isopropanol $K/NH_3/(CH_3)_2CHOH$

Carboxylic acids from α,β-ethylenecarboxylic acids $C{:}C \rightarrow CHCH$
Stereospecific hydrogenation
Sec. alcohols from ketones

67.



An aq. suspension of 2β,4b-dimethyl-1-carboxymethylene-2-methallyl-7-ethylenedioxy-1,2,3,4,4aα,4b,5,6,7,8,10,10aβ-dodecahydrophenanthrene-

4-one treated with 4 *N* NaOH, $NaBH_4$ dissolved in the resulting soln., kept at room temp. overnight, then heated 1 hr. at 100°, the resulting crude 4α-hydroxy acid suspended in liq. NH_3 at −80°, K added with rapid stirring, which is continued for 10 min., then dry 2-propanol added over a 5 min. period, the cooling bath removed, and stirring continued until the blue color is discharged → 2β,4b-dimethyl-1β-carboxymethyl-2-methallyl-7-ethylenedioxy-1,2,3,4aα,4β,5,6,7,8,10,10aβ-dodecahydrophenanthren-4α-ol. Y: 78%.—Prereduction of the 4-keto group gives an increased proportion of the 1β-dihydroacid and improves the combined yield. Other factors influencing the stereochemical course of the hydrogenation s. G. E. Arth et al., Am. Soc. *76*, 1715 (1954).

Zinc/acetic acid *Zn/CH_3COOH*

Hydrogenation of ethylene derivatives
s. *6*, 85

Ketones from ethyleneketones
s. *8*, 87

with simultaneous formation of ethylene derivatives from 1,2-dibromides
s. *8*, 938

α,β-Ethyleneketones from α,β:γ,δ-dienones via β,γ-ethyleneketones
s. *8*, 65

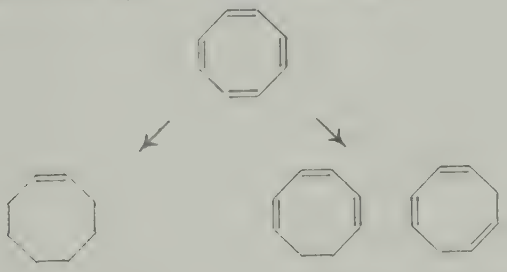
Zinc/acetic acid/pyridine *$Zn/CH_3COOH/C_5H_5N$*

Partial reduction of dienes to ethylene derivatives
s. *6*, 86

Zinc/platinum chloride/potassium hydroxide *$Zn/PtCl_4/KOH$*

Partial hydrogenation of cycloöctatetraenes

68.



Raney alloy added at 80-90° during 2 hrs. with vigorous stirring to 15 g. cycloöctatetraene and aq. 10%-NaOH → 15 g. crude cycloöctene.

2-3 drops aq. 4%-Pt-chloride added to a mixture of cycloöctatetraene, ethanol, Zn-dust, and KOH heated on a steam bath under N_2, and heating continued for 3 hrs. with occasional shaking → cycloöcta-1,3,5-triene. Y: ca. 85%.—Cycloöcta-1,3,6-triene is the main product, when aq. NaOH instead of KOH is used, and in aq.-alc. sulfuric acid.

W. G. Jones, Soc. *1954*, 1808.

Aluminum amalgam *Al,Hg*

Hydrogenation of (polyen)olesters
s. *7*, 774

Sodium boron hydride *$NaBH_4$*

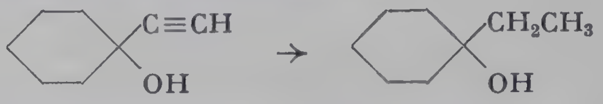
Alcohols from enolethers C:C(OAc) → CHCHOH
s. *8*, 66

Lithium aluminum hydride *$LiAlH_4$*

Nitroalkanes from nitroölefins C:C → CHCH
s. *9*, 87a

Hydrocarbons from acetylene derivatives C⋮C → CH_2CH_2

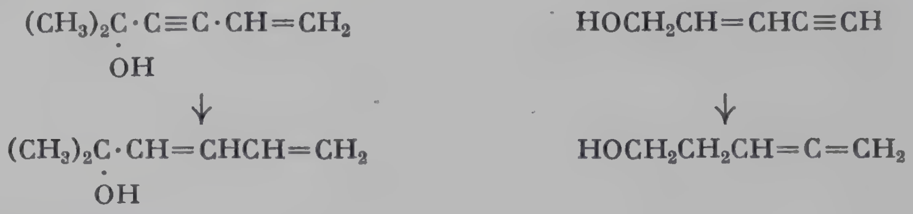
69.



A mixture of 1-ethynylcyclohexanol and $LiAlH_4$ in dioxane refluxed 18 hrs. → 1-ethylcyclohexanol. Y: 71%.—Less $LiAlH_4$ and a shorter reaction period gives 1-vinylcyclohexanol (cf. 70). E. B. Bates, E. R. H. Jones, and M. C. Whiting, Soc. *1954*, 1854.

trans-Ethylene from acetylene derivatives
s. *7*, 91

70.



$$\underset{OH}{(CH_3)_2C}\cdot C{\equiv}C\cdot CH{=}CH_2 \rightarrow \underset{OH}{(CH_3)_2C}\cdot CH{=}CHCH{=}CH_2$$

$$HOCH_2CH{=}CHC{\equiv}CH \rightarrow HOCH_2CH_2CH{=}C{=}CH_2$$

Dienes and allenes.

2-Methylhex-5-en-3-yn-2-ol added to a stirred suspension of $LiAlH_4$ in ether, and refluxed 3 hrs. → 2-methylhex-3,5-dien-2-ol. Y: 88%.

6.0 g. pent-2-en-4-yn-1-ol allowed to react with a small excess $LiAlH_4$ at 35° for 3 hrs. → 5.1 g. penta-3,4-dien-1-ol.

F. e., also dienes from diacetylene derivatives, s. E. B. Bates, E. R. H. Jones, and M. C. Whiting, Soc. *1954*, 1854; s. a. W. Oroshnik, Am. Soc. *76*, 5499 (1954); cf. Synth. Meth. *10*, 69, 84.

Hydrochalcols from chalcones C:C·CO → CH·CH·CHOH
s. *8*, 67

2-Ethylenealcohols ←
from α,β-acetylenecarboxylic acids
s. *9*, 111

2-Ethylenealcohols ←
from α,β-acetylenecarboxylic acid esters

71. $HC{\equiv}C\cdot CH_2CH_2\cdot C{\equiv}C\cdot COOC_2H_5 \rightarrow HC{\equiv}C\cdot CH_2CH_2CH{=}CHCH_2OH$

Selective hydrogenation. Ethyl 2,6-heptadiynoate in ether added to a stirred suspension of $LiAlH_4$ in ether, and refluxed 4.5 hrs. with stirring

→ 2-hepten-6-yn-1-ol. Y: 94%. B. L. Shaw and M. C. Whiting, Soc. *1954*, 3217.

γ-Hydroxyketones from α,β-ethylene-γ-diketones ←
s. *6*, 58

Amines from nitroethylene derivatives ←
Soxhlet extractor technique
s. *6*, 87

Partial ring hydrogenation ←
s. *7*, 82

Aluminum alkoxide *$Al(OR)_3$*

Selective reduction of cyclic unsatd. ketones
Ketones from α,β-ethyleneketones C:C → CHCH
s. *10*, 90

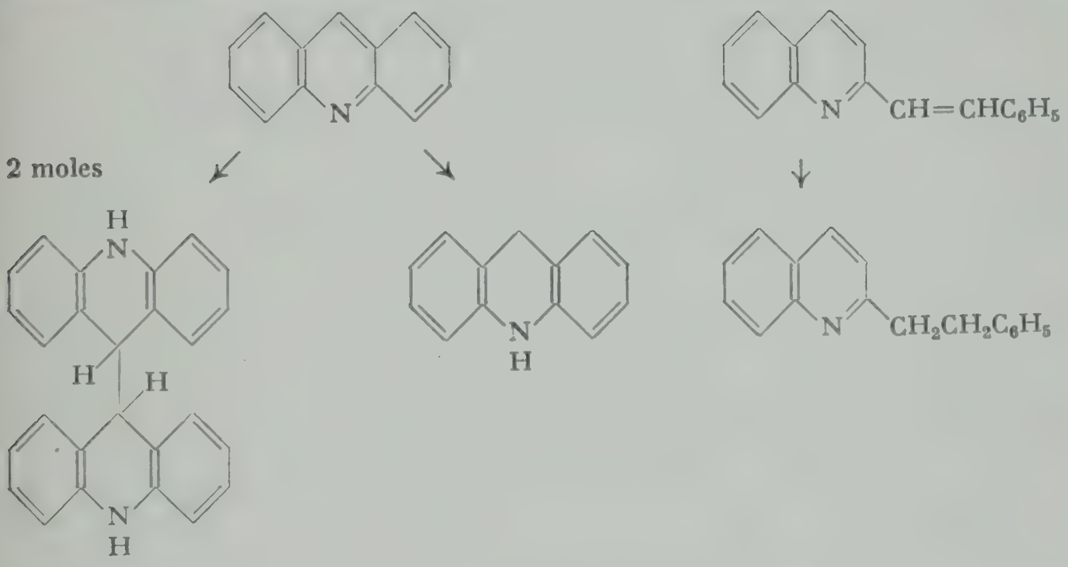
Formic acid *HCOOH*

Amines from enamines
s. *6*, 88

Mercaptans *RSH*

Reduction of conjugated azomethine systems
Reductive dimerization

72.



Acridine

heated with p-thiocresol

at 170-180° for 20 hrs. → biacridan (Y: 70.1%) and acridan (Y: 21.0%).

Benzalquinaldine

heated with p-thiocresol

at 200-215° for 24 hrs. → 2-(β-phenylethyl)quinoline. Y: 86.5% as the hydrochloride.

F. e. s. H. Gilman, J. L. Towle, and R. K. Ingham, Am. Soc. *76*, 2920 (1954).

Lead-palladium-calcium carbonate *Pb-Pd-$CaCO_3$*
s. Palladium-lead-calcium carbonate

Phosphorus *P*

Hydrogenation of ethylene derivatives
s. *6*, 762

Phosphorus/hydriodic acid *P/HI*

s. *8*, 68

α-Aminocarboxylic acids from thiazolidones
s. *6*, 269

Hydrosulfite $S_2O_4^{--}$

γ-Diketones from α,β-ethylene-γ-diketones
s. *9*, 88

Sulfuric acid/p-cymene ←

Hydrogen transfer ←
s. *7*, 83

Copper chromite $CuCr_2O_4$

Alcohols from ethylenecarboxylic acid esters ←
s. *6*, 109

Selective ring hydrogenation of N-heterocyclics ←
s. *7*, 84

Chromic acid—lithium/liq. ammonia $CrO_3—Li/NH_3$
s. Lithium/liq. ammonia—chromic acid

Cobaltic oxide/calcium oxide/sodium carbonate $Co_2O_3/CaO/Na_2CO_3$

Ring hydrogenation of amines ←
s. *8*, 69

Dicobalt octacarbonyl $Co_2(CO)_8$

Hydrogenation of ethylene derivatives C:C → CHCH
s. *6*, 89

Nickel *Ni*

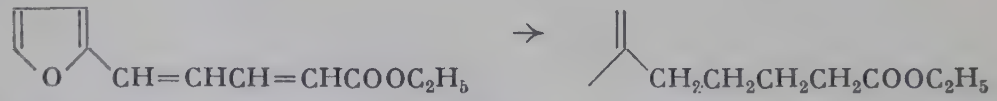
Poisoning of Raney-nickel by halides ←
s. *7*, 85

Partial hydrogenation of carbon-carbon double bonds C:C → CHCH
s. *8*, 70

of steroid polyenes
s. *9*, 89

Selective hydrogenation of carbon-carbon double bonds
s. *6*, 761

73.



of side chains of O-heterocyclics. Ethyl furfurylidenecrotonate hydrogenated with Raney-Ni in ethanol at room temp. and 80-100 atm. → ethyl furylvalerate. Y: 88-90%. W. Treibs and W. Heyer, B. *87*, 1197 (1954).

Ethylene from acetylene derivatives $C{:}C \rightarrow CH{:}CH$
cis-trans-Isomers s. *8*, 71

Amines from α,β-ethylenenitriles $C{:}C \cdot CN \rightarrow CHCH \cdot CH_2NH_2$
s. *8*, 795

1,1-Disulfones from 1,2-ethylene-1,1-disulfones $C{:}C \rightarrow CHCH$
s. *7*, 86

Ring hydrogenation, also partial ←
s. *7*, 98

Hydrogenation of O-heterocyclic rings
Furan derivatives s. *1*, 57/8; s. a. R. Paul and S. Tchelitcheff, Bl. *1953*, 1014

Hydrogenation of N-heterocyclic rings

γ-Hydroxypiperidines from γ-pyridones
s. *6*, 90

Piperidones from pyridones
s. *6*, 95

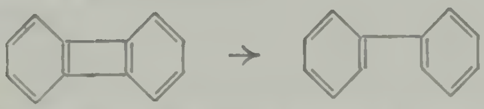
Selective hydrogenation

of halogeno-N-heterocyclics
s. *7*, 87

of cyclic quaternary ammonium salts
s. *6*, 91

Reductive ring opening of isocyclics C

74.



Ethanol and Raney-Ni satd. at room temp. and atmospheric pressure with H_2. diphenylene (prepn. s. 685) added, and hydrogenation continued for 4 hrs. until 1 equivalent of H_2 has been absorbed → diphenyl. Y: 85%. W. Baker, M. P. V. Boarland, and J. F. W. McOmie, Soc. *1954*, 1476.

Nickel/sodium hydroxide *Ni/NaOH*
Hydrogenation of ethylene derivatives $C{:}C \rightarrow CHCH$
s. *8*, 72

Nickel/copper *Ni/Cu*
cis-Ethylene from acetylene derivatives $C{:}C \rightarrow CH{:}CH$
s. *8*, 71

Nickel/aluminum *Ni,Al*
Partial hydrogenation of cyclooctatetraenes $C{:}C \rightarrow CHCH$
s. *10*, 68

Nickel-silica $Ni\text{-}SiO_2$

Deuteration of olefins ←

75. Because of redistribution of H- and D-atoms, catalytic deuteration is of limited utility in the prepn. of specific deuterated hydrocarbons. J. N. Wilson et al., Ind. Eng. Chem. *45*, 1480 (1953).

Ring hydrogenation ←

Benzene rings
s. *9*, 92

Phenols
s. *7*, 88

Ruthenium-carbon $Ru\text{-}C$

s. *7*, 89

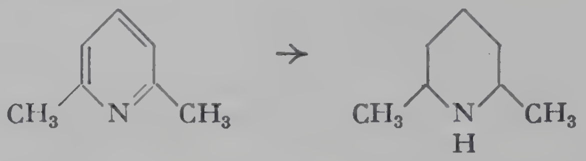
Ruthenium dioxide RuO_2

of amines
s. *9*, 93

Rhodium-alumina $Rh\text{-}Al_2O_3$

of N-heterocyclics

76.



A soln. of 2,6-lutidine in glacial acetic acid hydrogenated with 5%-Rh-on-alumina at 60° and 3 atm. until the theoretical amount of H_2 has been absorbed → *cis*-2,6-dimethylpiperidine. Y: 88.5%.—Longer times were required with PtO_2. F. e. s. C. G. Overberger et al., Am. Soc. *77*, 4100 (1955).

Palladium Pd

Selective hydrogenation of O-heterocyclics
s. *7*, 90

Palladium-calcium carbonate $Pd\text{-}CaCO_3$

Hydrogenation of acetylene derivatives ←
s. *9*, 101

Ethylene from acetylene derivatives $C\vdots C \rightarrow CH{:}CH$
cis-trans-Isomers s. *7*, 91

Partial ring hydrogenation ←
s. *7*, 92

Selective hydrogenation ←
s. *8*, 73

Palladium-calcium carbonate/pyridine $Pd\text{-}CaCO_3/C_5H_5N$

Selective and partial hydrogenation

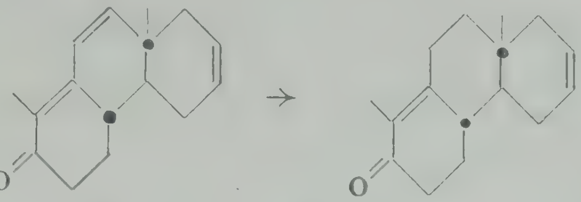
Ethylene from acetylene derivatives $C\vdots C \rightarrow CH{:}CH$
s. *6*, 92; s. a. A. Sandoval et al., Am. Soc. *77*, 148 (1955)

Palladium-strontium carbonate $Pd\text{-}SrCO_3$

s. *8*, 74 $C{:}C \rightarrow CHCH$

Palladium-strontium carbonate-sodium hydroxide *Pd-SrCO$_3$/NaOH*

77.



Total synthesis of steroids. (–)-1,14-Dimethyl-2-keto-$\Delta^{1(11)6,9}$-octahydrophenanthrene added to prereduced 2%-Pd-on-SrCO$_3$ in isopropanol to which 10%-NaOH soln. has been added, vigorously agitated at 25° and exactly 2 moles H$_2$ carefully metered into the flask through a Precision Wet Test Meter during 38 min. → (–)-1,14-dimethyl-2-keto-$\Delta^{1(11),6}$-decahydrophenanthrene. Y: ca. 100%.—This technique avoids the use of the acid sensitive acetonide group during the synthesis of ring A of the steroid skeleton.—Also racemate s. L. B. Barkley et al., Am. Soc. *76*, 5014 (1954).

Palladium-carbon *Pd-C*

Ketones from ethyleneketones
Stereochemistry of steroids
s. *9*, 94

Ethylene from acetylene derivatives C⋮C → CH:CH
s. *9*, 95

Selective hydrogenation

α-Alkyl-β-ketocarboxylic acid esters C:C → CHCH
from α-alkylidene-β-ketocarboxylic acid esters
s. 7, 797

s. *9*, 96 C⋮C → CH_2CH

1,2-Dideutero compounds from ethylene derivatives C:C → CDCD
s. 7, 93

Selective hydrogenation of N-heterocyclics ←
with replacement of chlorine by hydrogen
s. 7, 87

Palladium-carbon/sodium hydroxide *Pd-C/NaOH*

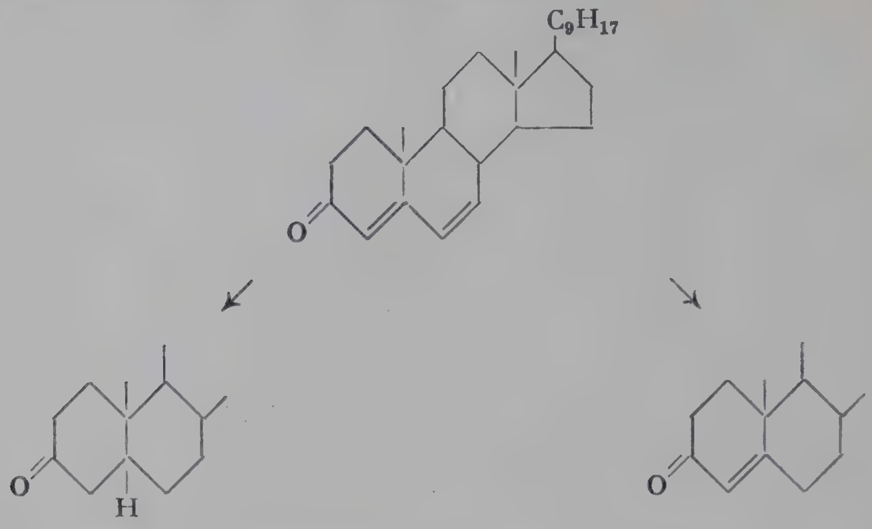
Carboxylic acids from α,β-ethylenecarboxylic acids C:C → CHCH
Hydrocoumarins from coumarins via coumaric acids
s. 8, 75

Palladium-carbon/potassium hydroxide *Pd-C/KOH*

Ketones from α,β-ethyleneketones
cis-trans-Isomers s. 7, 94

Total and partial selective hydrogenation

78.



Isoergosterone (prepn. s. 552)

and KOH in dry ethanol hydrogenated with freshly prepared 10% palladized charcoal until after 40 min. 2 moles of H_2 have been absorbed → 5β-ergost-22-en-3-one. Y: almost 100% (Soc. *1954*, 1302). Soc. *1954*, 2627, Y: 80%.

1 g. dissolved in dry ether, liq. NH added with stirring, then Li added i small pieces during 5 min., after a fur ther 10 minutes' stirring abs. ethano added dropwise so that the soln. becomes colorless after 15-20 min. - 0.8 g. ergosta-4,22-dien-3-one (Soc. *195* 2627). (Soc. *1954*, 1302: 0.6 g., same reagents, different procedure.)

F. Johnson, G. T. Newbold, and F. S. Spring, Soc. *1954*, 1302; A. F Daglish, J. Green, and V. D. Poole, Soc. *1954*, 2627.

Palladium-carbon/piperidine *Pd-C/C_5H_{11}*

Ketones from α,β-ethyleneketones
Partial hydrogenation of carbon-carbon double bonds
s. *8*, 76

Palladium-lead-calcium carbonate *Pd-Pb-CaCO*

Ethylene from acetylene derivatives C⋮C → CH:C

s. *7*, 95; s. a. W. Oroshnik and A. D. Mebane, Am. Soc. *76*, 5719 (1954) M. G. Ettlinger and J. E. Hodgkins, Am. Soc. *77*, 1831 (1955); L Crombie and A. G. Jacklin, Soc. *1955*, 1740; J. L. H. Allan, E. R. H Jones, and M. C. Whiting, Soc. *1955*, 1862; B. W. Baker, R. P. Lin stead, and B. C. L. Weedon, Soc. *1955*, 2218

Palladous oxide *Pd*

Selective hydrogenation ←
s. *7*, 96

Palladium hydroxide-calcium carbonate *$Pd(OH)_2$-$CaCO_3$*

Hydrogenation of enolacetates $C{:}C(OAc) \rightarrow CHCH(OAc)$
s. *6*, 93

Platinum oxide *PtO_2*

Hydrogenation of carbon-carbon double bonds $C{:}C \rightarrow CHCH$
s. *8*, 77

Amines from ethyleneamines
s. *8*, 78

Nitro compounds from nitroethylene derivatives
s. *8*, 79

Ethylene derivatives from dienes
s. *7*, 97

with migration of a carbon-carbon double bond
s. *8*, 80

Partial hydrogenation of steroid polyenes
s. *9*, 90

Hydrogenation of a carbon-carbon double bond
with protection of another carbon-carbon double bond
s. *9*, 97

Hydrocarbons from acetylene derivatives ←
s. *9*, 101

Hydrocarbons from enolesters ←
trans-Hydrogenation s. *6*, 94

Sec. alcohols from ethyleneketones via ketones ←
Stereochemistry of steroids
s. *8*, 81

Hydrogenation of benzene rings $C{:}C \rightarrow CHCH$
s. *9*, 931

Controlled partial ring hydrogenation
s. *7*, 98

Selective hydrogenation of carbon-carbon double bonds

in isocyclics
s. *8*, 82

in N-heterocyclics
s. *9*, 98

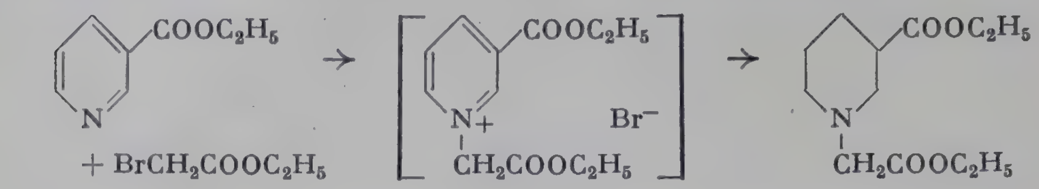
Piperidones from pyridones
s. *6*, 95

Selective benzene ring hydrogenation
of condensed N-heterocyclics
s. *9*, 99

Selective hydrogenation ←
of cyclic quaternary ammonium salts
s. *6*, 91

N-Subst. piperidines from pyridines via pyridinium salts ←

79.



A mixture of ethyl nicotinate, ethyl bromoacetate, and alcohol stirred with cooling when the temp. rises above 70°, the crude reaction mixture containing the quaternary ammonium salt diluted with warm ethanol, and hydrogenated with PtO_2 at room temp. and 70 atm. → ethyl 3-carbethoxypiperidine-1-acetate. Y: 75%. F. e. s. L. H. Sternbach and S. Kaiser, Am. Soc. *74*, 2215 (1952).

Disubst. succinic acids from fumaric di-γ-enollactones C
s. *8*, 83

Platinum oxide/potassium hydroxide *PtO_2/KOH*

Partial and selective hydrogenation of carbon-carbon double bonds C:C → CHCH
s. *9*, 100

Platinum oxide/iodine/sodium hydroxide *$PtO_2/I/NaOH$*

Hydrogenation of N-heterocyclic rings ←
Partial hydrogenation of cyclic quaternary ammonium salts
s. *6*, 96

Platinum oxide/perchloric acid *$PtO_2/HClO_4$*

Alcohols from ethylenealcohols C:C → CHCH
Large scale hydrogenation s. *7*, 99

Platinum oxide/palladium *PtO_2/Pd*

Hydrogenation of ethylene derivatives
s. *6*, 97

Platinum chloride/zinc/potassium hydroxide *$PtCl_4/Zn/KOH$*
s. Zinc/platinum chloride/potassium hydroxide

Via intermediates *v.i.*

Hydrogenation of the double bond of quaternary ethyleneammonium salts
Exchange of the halogen anion
s. *8*, 84

Hydrogenation of acetylene derivatives C⋮C → CH_2CH_2
s. *9*, 101

Rearrangement

Hydrogen/Oxygen Type HC↶HO

Ethyl malonate *$H_2C(COOC_2H_5)_2$*
Isoglycosamines via glycosamines ←
Amadori rearrangement
s. *8*, 85

Dowex-50
Resins as catalysts ←
α,β-Ethyleneketones and α-hydroxyketones from α,β-acetylenealcohols ←
s. *9*, 102

Sulfuric acid *H_2SO_4*
α,β-Ethyleneketones from α,β-acetylenealcohols ←
s. *6*, 98

Exchange

Oxygen ↑ HC⇵O

Electrolysis ↯
Cyclic imines from dicarboxylic acid imides ←
s. *7*, 110

Electrolytic reduction of α-aminoketones ↻
Ring opening s. *7*, 100

Sodium *Na*
Replacement of alkoxyl by hydrogen OR → H
s. *6*, 99; *7*, 107

Hydrocarbons and sec. alcohols from ketones CO ↗ CHOH, CO ↘ CH_2
s. *7*, 101

β-Hydroxyketones from β-ketocarboxylic acid esters ←
s. *6*, 216

Reduction of N-heterocyclics ←
s. *8*, 86; *9*, 557

Lactones from ketocarboxylic acids ○
s. *9*, 103

Alcohols from m-dioxanes ↻
s. *7*, 730

Sodium/liq. ammonia *Na/NH_3*
Replacement of alkoxyl by hydrogen OR → H
s. *7*, 107

Reductive cleavage of ethers ↻
s. *6*, 99

Lithium iodide/sodium boron hydride *$LiI/NaBH_4$*
s. Sodium boron hydride/lithium iodide

Cupric oxide *CuO*

Alcohols from carboxylic acids COOH → CH_2OH

s. *3*, 51; diols from dicarboxylic acids s. Helv. *38*, 976 (1955)

Zinc *Zn*

Replacement of acoxy groups by hydrogen OAc → H

s. *9*, 104

Zinc/sodium hydroxide *Zn/NaOH*

o-Diphthalides from oxido-o-diphthalides ←

s. *8*, 205

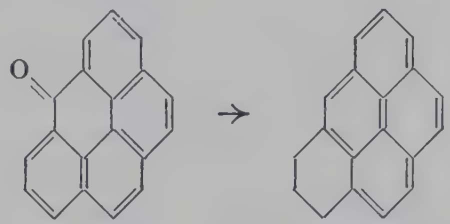
Zinc/cupric sulfate/ammonia *Zn/CuSO₄/NH₃*

Hydrocarbons from ketones CO → CH_2

s. *9*, 105

Zinc/zinc chloride/sodium chloride *Zn/ZnCl₂/NaCl*

80.

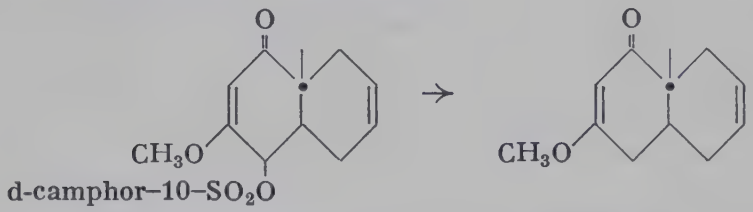


NaCl and moist $ZnCl_2$ added to an intimate mixture of 1 g. naphthanthrone and Zn-dust, the mixture melted, and the temp. raised over 15 min. to 300° with stirring → 0.8 g. 2,3-trimethylenepyrene. E. Clar and D. G. Stewart, Am. Soc. *75*, 2667 (1953).

Zinc/acetic acid *Zn/CH₃COOH*

Hydrocarbons from sulfonic acid esters OSO_2R → H

81.



Zn-dust added with vigorous agitation to a suspension of (–)-*trans*-1-Hydroxy-4-keto-2-methoxy-10-methyl-$\Delta^{2,6}$-hexahydronaphthalene d-camphor-10-sulfonate (prepn. s. 123) in 99.5%-acetic acid containing some acetic anhydride, the temp. carefully raised to 60-80°, then allowed to rise to 100° without external heating, and kept 2 hrs. at 100-110° first by occasional cooling, then by gentle heating → (–)-*trans*-4-keto-2-methoxy-10-methyl-$\Delta^{2,6}$-hexahydronaphthalene (startg. m. f. 57). Y: 90-92%. F. e. s. A. J. Speziale, J. A. Stephens, and Q. E. Thompson, Am. Soc. *76*, 5011 (1954).

Ketones from oxidoketones and ethyleneketones ←

s. *8*, 87

Zinc and stannous chloride s. Stannous chloride and zinc *Zn and SnCl₂*

Zinc amalgam *Zn,Hg*

Hydrocarbons from trihalogenomethyl ketones $COCHal_3 \rightarrow CH_2CH_3$
s. *8*, 115

Amines from α-aminoketones with rearrangement ←
Clemmensen reduction – Ring contraction and expansion
s. *6*, 100

Zinc amalgam/platinum oxide *Zn,Hg/PtO₂*

Hydrocarbons from acyloins $COCHOH \rightarrow CH_2CH_2$
s. *9*, 931

tert-Butylmagnesium chloride *$(CH_3)_3C \cdot MgCl$*

Replacement of alkoxy groups by hydrogen $OR \rightarrow H$
s. *10*, 316

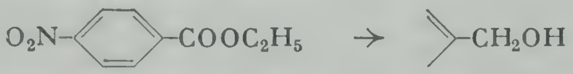
Zinc chloride/mercaptan s. Mercaptan/zinc chloride *$ZnCl_2/RSH$*

Cadmium-nickel salt/copper chromite ←
s. Copper chromite/cadmium-nickel salt

Lithium boron hydride *$LiBH_4$*

Alcohols from carboxylic acid esters $COOR \rightarrow CH_2OH$

82.



Ethyl p-nitrobenzoate allowed to react 4 hrs. with *$LiBH_4$-dioxane complex* in tetrahydrofuran at 20° → p-nitrobenzyl alcohol. Y: 88%.—The complex of $LiBH_4$ with dioxane is less sensitive to humidity. F. e., prepn. of $LiBH_4$ and the complex, s. R. Paul and N. Joseph, Bl. *1953*, 758.

Alkylamines from acylamines $NCOR \rightarrow NCH_2R$
s. *9*, 113; also, more conveniently, with $LiBH_4$ s. M. Bory and C. Mentzer, Bl. *1953*, 814

Lactones from ketocarboxylic acids ○
s. *6*, 53

Sodium boron hydride *$NaBH_4$*

$NaBH_4$ as reducing agent in the sugar series ←
s. *8*, 45

Reductive cleavage of N-heterocyclic ozonides ←
s. *9*, 106

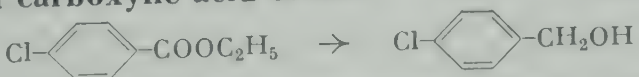
Sodium boron hydride/lithium iodide *$NaBH_4/LiI$*

Diols from ketocarboxylic acid esters
s. *9*, 876

Reductions with
Sodium boron hydride/aluminum chloride *$NaBH_4/AlCl_3$*

Alcohols from carboxylic acid esters $COOR \rightarrow CH_2OH$

83.



A stirred soln. of $NaBH_4$ in diethylene glycol dimethyl ether and ethyl p-chlorobenzoate treated slowly below 50° with a soln. of $AlCl_3$ in the same solvent, finally heated a few min. on a steam bath to complete the reaction → p-chlorobenzyl alcohol. Y: 84-89%.—Also carboxylic acids and nitriles are rapidly reduced at room temp. Nitro and amide groups are not affected. H. C. Brown and B. C. Subba Rao, Am. Soc. *77*, 3164 (1955).

Lithium aluminum hydride *$LiAlH_4$*

Ethylenimines from 2-alkoxyethylenimines OR → H
s. *9*, 242

Hydrocarbons from methylsulfonic acid esters ←
Sec. alcohols from ketones

s. *9*, 109; hydrocarbons s. a. A. W. Schrecker and J. L. Hartwell, Am. Soc. *77*, 432 (1955)

Hydrocarbons from p-toluenesulfonic acid esters OTs → H
s. *6*, 47; *8*, 88; retention of steric configurations s. K. Alder and W. Roth, B. *88*, 407 (1955); A. W. Schrecker and J. L. Hartwell, Am. Soc. *77*, 432 (1955)

Anomalous reductions with $LiAlH_4$ to hydrocarbons ←
from oxo compounds s. *9*, 107; also from carboxylic acids and esters. hydroxy and alkoxy compounds s. Can. J. Chem. *31*, 775 (1953)

Hydrocarbons from carboxylic acids COOH → CH_3
via alcohols and halides
s. *9*, 108

Cyclohexenones from 1,3-cyclohexanediones ←
via 1-methoxy-1-cyclohexen-3-ones
s. *8*, 89

Alcohols from oxido compounds ←
with simultaneous formation of
hydrocarbons and alcohols
from p-toluenesulfonic acid esters
s. *8*, 90

Alcohols from ozonides ←
s. *10*, 149

Alcohols from carboxylic acid esters COOR → CH_2OH
s. *6*, 101; 1,3-diols s. H. L. Lochte and E. N. Wheeler, Am. Soc. *76*, 5548 (1954); also from acid chlorides s. B. O. Field and J. Grundy, Soc. *1955*, 1110

84. $C_6H_5C{\equiv}C\cdot COOCH_3 \rightarrow C_6H_5C{\equiv}C\cdot CH_2OH$

Acetylenealcohols. Methyl phenylpropiolate added dropwise at −78° to a soln. of $LiAlH_4$ in ether, after 5 min. water added, and the mixture allowed to reach room temp. → phenylpropargyl alcohol. Y: 96%.—*trans*-Cinnamyl alcohol is obtained with excess reagent at 20° (cf. 70). E. B. Bates, E. R. H. Jones, and M. C. Whiting, Soc. *1954*, 1854.

Hydroxyacetals from carbalkoxyacetals
s. *8*, 91

Oxidoalcohols from oxidocarboxylic acid esters
s. *8*, 92

Alcohols from acyl peroxides $(\mathrm{RCOO})_2 \rightarrow 2\,\mathrm{RCH_2OH}$
s. *9*, 6

Reduction of enolizable β-dioxo compounds to ethylenealcohols ←
s. *9*, 110

2-Ethylenealcohols

from α,β-acetylenecarboxylic acid esters ←
s. *9*, 111; *10*, 71

from α,β-dibromocarboxylic acid esters ←
s. *10*, 687

Diols from aldehydocarboxylic acid esters ←
s. *7*, 104

1,3-Diols $\mathrm{CO{\cdot}C{\cdot}COOR} \rightarrow \mathrm{CH(OH){\cdot}C{\cdot}CH_2OH}$
from β-ketocarboxylic acid esters
s. *8*, 93

Aldehydes from carboxylic acids and esters $\mathrm{COOR} \rightarrow \mathrm{CHO}$
Inverse addition s. *9*, 112

Acetals from orthocarboxylic acid esters $\mathrm{C(OR)_3} \rightarrow \mathrm{CH(OR)_2}$
s. *8*, 94

Lactones and diols ←
from dicarboxylic acid anhydrides
Sterically hindered compounds s. *7*, 105

Alkylation of amines via acylamines $\mathrm{CON}\langle \rightarrow \mathrm{CH_2N}\langle$

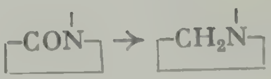
N-Methylation s. *9*, 113; alkylamines from acylamines, also, more conveniently, with $\mathrm{LiBH_4}$ s. M. Bory and C. Mentzer, Bl. *1953*, 814

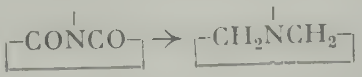
Amines from carboxylic acid amides
s. *7*, 106, 461; *9*, 524; *10*, 92; cf. *8*, 32

with rearrangement
s. *8*, 770

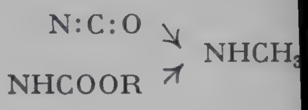
Amines from cyanoketocarboxylic acid esters ←
s. *10*, 60

Cyclic imines

from lactams

$-\mathrm{CO}\overset{|}{\mathrm{N}}- \rightarrow -\mathrm{CH_2}\overset{|}{\mathrm{N}}-$
s. *6*, 102; *7*, 107; quinolizidine derivatives
s. K. T. Potts and R. Robinson, Soc. *1955*, 2675

from dicarboxylic acid imides

$-\mathrm{CO}\overset{|}{\mathrm{N}}\mathrm{CO}- \rightarrow -\mathrm{CH_2}\overset{|}{\mathrm{N}}\mathrm{CH_2}-$
s. *6*, 103

Methylamines from urethans and isocyanates



$$\begin{matrix} N{:}C{:}O \searrow \\ NHCOOR \nearrow \end{matrix} NHCH$$

s. *8*, 95; from urethans s. a. R. L. Dannley, M. Lukin, and J. Shapiro, J. Org. Chem. *20*, 92 (1955)

←

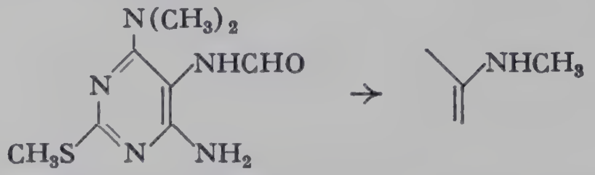
Aminoalcohols
from dicarboxylic acid monoamides
and dicarboxylic acid amide esters

s. *9*, 114

Lithium aluminum hydride/pyridine *$LiAlH_4/C_5H_5N$*

Amines from carboxylic acid amides $CON\langle \rightarrow CH_2N\langle$

85.



A warm soln. of 2-methylmercapto-4-amino-5-formamido-6-dimethylaminopyrimidine in dry pyridine added during 10 min. above the center of a refluxing ethereal soln. of $LiAlH_4$, and refluxing continued for 2 hrs. → 2-methylmercapto-4-amino-5-methylamino-6-dimethylaminopyrimidine. Y: 79%.—The Soxhlet extraction procedure for the reduction of ether-insoluble compounds was unsuccessful. F. e. s. B. R. Baker, R. E. Schaub, and J. P. Joseph, J. Org. Chem. *19*, 638 (1954).

Aluminum alkoxide *$Al(OR)_3$*

Meerwein-Ponndorf-Verley reduction ○
Lactones from ketocarboxylic acid esters

s. *6*, 104; *9*, 115

Aluminum chloride/sodium boron hydride *$AlCl_3/NaBH_4$*
s. Sodium boron hydride/aluminum chloride

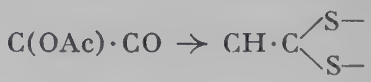
Formic acid/formaldehyde *$HCOOH/H_2CO$*

Methylamines from formamides $NCHO \rightarrow NCH_3$

s. *9*, 116

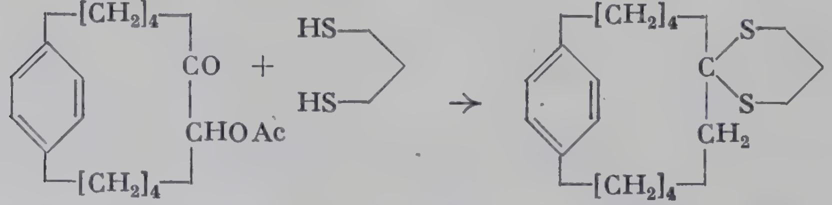
Mercaptans/zinc chloride *$RSH/ZnCl_2$*

Mercaptals from α-acoxyketones



$$C(OAc)\cdot CO \rightarrow CH\cdot C\begin{matrix} \diagup S- \\ \diagdown S- \end{matrix}$$

86.



5-Acetoxy-6-keto[10]paracyclophane, 1,3-propanedithiol, and powdered freshly fused $ZnCl_2$ stirred in dry benzene, dry HCl passed in until a red oil separates, and stirred 2 additional hrs. at room temp. → 5-keto-[10]paracyclophane trimethylenemercaptal. Y: 83%. F. e. s. D. J. Cram and M. Cordon, Am. Soc. *77*, 1810 (1955).

Stannous chloride and zinc — *$SnCl_2$ and Zn*

Anthracenes from anthraquinones ←
s. *6*, 105

Hydrazine/potassium hydroxide — *$H_2N{\cdot}NH_2/KOH$*

Hydrocarbons from carboxylic acid esters with simultaneous formation of amines from nitro compounds $COOR \rightarrow CH_3$
s. *7*, 36

Phosphorus/potassium iodide — *P/KI*

Lactones from ketocarboxylic acids ○
s. *7*, 108

Hydrosulfite — *$S_2O_4^{--}$*

Anthrones from anthraquinones $CO \rightarrow CH_2$
s. *6*, 106

Copper chromite — *$CuCr_2O_4$*

Hydrocarbons from aldehydes via prim. alcohols $CHO \rightarrow CH_2OH \rightarrow CH_3$
s. *6*, 107

Alcohols and hydrocarbons from oxo compounds ←
s. *6*, 108

Alcohols from carboxylic acid esters $COOR \rightarrow CH_2OH$
s. *9*, 567

Alcohols from ethylenecarboxylic acid esters ←
s. *6*, 109

Lactams from dicarboxylic acid imides $\underbrace{-CO\overset{|}{N}CO-} \rightarrow \underbrace{-CH_2\overset{|}{N}CO-}$
s. *7*, 110

Hydrogenolysis of O-heterocyclics C
s. *8*, 96

Alcohols from ethylene derivatives via m-dioxanes
Synthesis with addition of 1 C-atom
s. *7*, 109

Copper chromite/cadmium-nickel salt ←

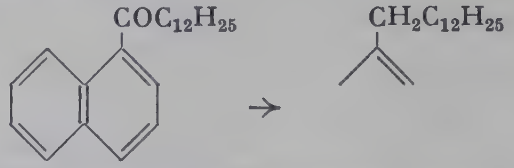
Alcohols from carboxylic acids $COOH \rightarrow CH_2OH$

87. **Labeled compounds.** Cd-Ni-propionate-1-C^{14}, prepared from the acid with a Cd-Ni-hydroxide slurry, hydrogenated 9 hrs. with $CuCr_2O_4$ at 240° and 235 atm. → propanol-1-C^{14}. Y: 94%.—The method is suitable for small scale prepn. F. e. s. P. T. Adams, R. E. Selff, and B. M. Tolbert, Am. Soc. *74*, 2416 (1952).

Copper chromite/palladium-carbon *$CuCr_2O_4/Pd$-C*

Hydrocarbons from ketones $CO \rightarrow CH_2$

88.



n-Dodecyl 1-naphthyl ketone hydrogenated with Cu-chromite for 4 hrs. at 200-230° at a maximum pressure of 160 atm., then for 15 min. at 250°, the crude product heated with Pd-charcoal to 200°, then the temp. raised during 4 hrs. to 280°, finally heated 10 min. at 300° in a slow N_2-stream → 1-tridecylnaphthalene. Y: 80-90%. —Dehydrogenation is necessary to eliminate nuclear reduction. F. e. s. D. G. Anderson, J. C. Smith, and R. J. Rallings, Soc. *1953*, 443.

Perchloric acid/palladium-carbon *$HClO_4/Pd$-C*
s. Palladium-carbon/perchloric acid

Cobalt(II) acetate *$(CH_3COO)_2Co$*

Hydrocarbons from ketones
s. *8*, 97

Nickel *Ni*

Hydrocarbons from p-toluenesulfonic acid esters ArOTs → ArH
s. *6*, 9

Lactones from ketocarboxylic acids ○
s. *7*, 111

Nickel/sodium carbonate *Ni/Na_2CO_3*

Carboxylic acid esters OAc → H
from α-acoxycarboxylic acid esters
with simultaneous formation of amines from nitro compounds
s. *6*, 110

Ruthenium dioxide and ruthenium-carbon *RuO_2 and Ru-C*

Alcohols from carboxylic acids $COOH \rightarrow CH_2OH$

89. $CH_2OHCOOH \rightarrow CH_2OHCH_2OH$

Ru-catalysts can be used for the direct hydrogenation of carboxylic acids to the corresponding alcohols in good yields at temp. of ca. 150°. —E: Glycolic acid in water hydrogenated 0.16 hr. with water-washed RuO_2 at 145-149° and 700-775 atm. → ethylene glycol. Y: 83%. F. e. s. J. E. Carnahan et al., Am. Soc. *77*, 3766 (1955).

Palladium *Pd*

Partial replacement of acoxy groups by hydrogen
s. *7*, 112

Phenols from hemiquinols ←
s. *7*, 206

Palladium-barium sulfate *Pd-$BaSO_4$*

Hydrocarbons from ketones $CO \rightarrow CH_2$
s. *9*, 117

Palladium-carbon *Pd-C*

Ketones from diketones with different reactivity of the keto groups
s. *7*, 113

Carboxylic acids from C:C(OH)COOR → $CHCH_2COOH$
***α,β*-ethylene-*α*-hydroxycarboxylic acid esters**
s. *9*, 118

Prim. amines from sec-aminoketones ←
s. *8*, 487

Amines and nitriles from cyanocarbonates ←
Directing the hydrogenation by acids
s. *6*, 111

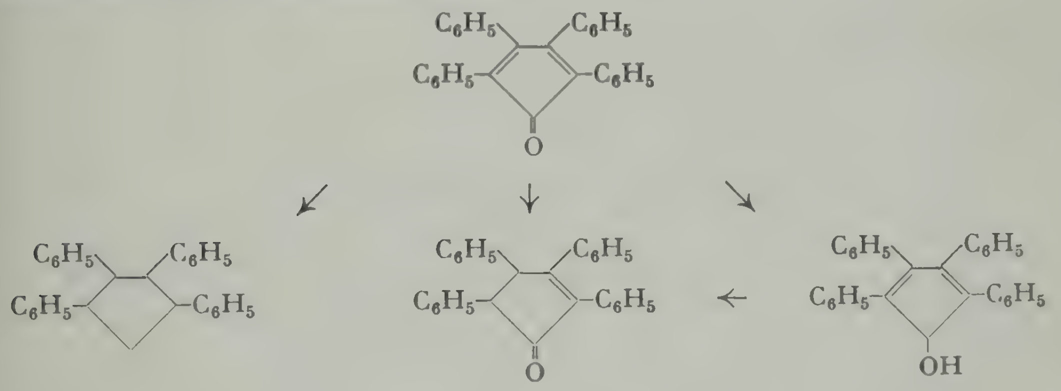
Palladium-carbon/copper chromite *$Pd\text{-}C/CuCr_2O_4$*
s. Copper chromite/palladium-carbon

Palladium-carbon/perchloric acid *$Pd\text{-}C/HClO_4$*
Hydrocarbons from ketones CO → CH_2
s. *7*, 114

Platinum *Pt*

Total and selective reduction of cyclic unsatd. ketones ←
Ketones from 2-ethylenealcohols

90.



Tetracylone

A satd. soln. of tetracylone in acetic acid hydrogenated with Pt-black at room temp. and 40 p. s. i. for 45 min. → tetraphenylcyclopentane. Y: 85%.

and Al-isopropoxide added to a mixture of isopropanol and dry toluene distilled slowly for 2 hrs., toluene added, and distillation continued until after 2 hrs. no more acetone is detected.

dissolved in n–butyl ether, treated at 0–10° with a soln. of $LiAlH_4$ in diethyl ether, and stirred 3 hrs. → 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ol (Y: 81%) refluxed 0.5 hr. in acetic acid containing a little Zn-dust.

↘ ↙

(Y: 86%) 2,3,4,5-tetraphenylcyclopenta-2-en-1-one. (Y: 96%)

F. reductions, also anomalous product by Wolff-Kishner reduction, and isomerization, also with Al-isopropoxyde, s N. O. V. Sonntag et al., Am. Soc. *75*, 2283 (1953).

Platinum oxide *PtO_2*

Replacement of alkoxy groups by hydrogen OR → H
s. *10*, 316

Hydrocarbons from enolesters ←
s. *6*, 94

Coumarans from 3-acoxybenzofurans
s. *7*, 115

Hydrocarbons from ketones $CO \rightarrow CH_2$
s. *6*, 113

Ethylene derivatives from enol acetates C:C(OAc) → C:CH
s. *6*, 114

Reductive ring contraction ←
s. *6*, 115

Platinum oxide/zinc amalgam *PtO_2/Zn,Hg*
s. Zinc amalgam/platinum oxide

Platinum oxide/hydrochloric acid *PtO_2/HCl*

Ring hydrogenation of phenols ←
s. *8*, 98

Via intermediates *v.i.*

Hydrocarbons from tosylates via thiocyanates OTs → H
s. *7*, 621

Hydrocarbons from ketones via sec. alcohols $CO \rightarrow CHOH \rightarrow CH_2$
s. *8*, 99

Hydrocarbons from oxo compounds via hydrazones $CO \rightarrow CH_2$
Wolff-Kishner reduction

of 11-ketosteroids
s. *8*, 100

with migration of carbon-carbon double bonds
s. *6*, 117

Carboxylic acids from α-ketocarboxylic acids $COCOOH \rightarrow CH_2COOH$
s. *10*, 195

Simplified procedures $CO \rightarrow CH_2$
of the Wolff-Kishner reduction
Huang Minlon modification

s. *6*, 116; *8*, 101; thiophene derivatives s. G. M. Badger, H. J. Rodda, and W. H. F. Sasse, Soc. *1954*, 4162

Hydrocarbons from aldehydes $CHO \rightarrow CH_3$
s. *8*, 836

Hydrocarbons
from sterically hindered ketones

91. Sterically hindered ketones can be reduced by the Huang-Minlon modification of the Wolff-Kishner reduction if completely anhydrous hydrazine is used and all water kept, so far as possible, out of the reaction system, whereby the reducing power is remarkably improved. E. s. D. H. R. Barton, D. A. J. Ives, and B. R. Thomas, Soc. *1955*, 2056.

Acetals from ketoacetals $CO \rightarrow CH_2$
s. *9*, 119

Carboxylic acids from ketocarboxylic acids
s. *8*, 102

with preceding acid cleavage
s. *9*, 228

Carboxylic acids from cyanoketones
s. *8*, 103

Dicarboxylic acids
from cyanoketocarboxylic acid esters
s. *10*, 141

Two-step procedure
s. *9*, 120

Lock modification
s. *2*, 96; reduction of ar. hydroxyoxo compounds s. M. *85*, 802 (1954); carboxylic from α-ketocarboxylic acids s. B. *88*, 564 (1955)

Thioöxindoles from thianaphthenequinones ←
via o-mercaptophenylacetic acids
s. *9*, 121

Simplified Wolff-Kishner reduction $CO \rightarrow CH_2$
with simultaneous decarbalkoxylation
Decarboxylation by azeotropic distillation
Pyrroles
s. *9*, 122

Reduction of oxo to hydrocarbon groups
with simultaneous formation of
amines from nitro compounds
s. *9*, 123

Hydrocarbons from ketones via cyclic mercaptals
s. *7*, 627; ketones from diketones s. A. T. Blomquist, J. Prager, and J. Wolinsky, Am. Soc. *77*, 1804 (1955)

Carboxylic acid esters from
α- and β-ketocarboxylic acid esters via mercaptals
s. *7*, 116

Hydrocarbons from quinones via dioximes and diamines ←
s. *7*, 117

α,β-Ethylenealdehydes from α-hydroxymethyleneketones
via α-alkoxymethyleneketones ←
s. *7*, 118

Prim. alcohols from carboxylic acids COOH → CH_2OH
via carboxylic acid chlorides
s. *8*, 104

Nitrogen ↑ HC⇵N

Irradiation/alkyl nitrite s. Alkyl nitrite/irradiation ←

Sodium *Na*
Aldehydes from carboxylic acid hydrazides $CONHNH_2 \rightarrow CHO$
s. *9*, 124

Sodium amalgam *Na,Hg*
Reductive cleavage of quaternary ammonium salts $CH_2\overset{+}{N}\!\lessgtr \rightarrow CH_3$
Emde degradation
s. *8*, 105

Potassium hydroxide *KOH*
o-Mercaptophenylacetic acids
from thianaphthenequinone 3-hydrazones
s. *9*, 121

Sodium/alcohol *NaOR*
Hydrocarbons from tert. amines $CH_2N\!\lessgtr \rightarrow CH_3$
s. *8*, 827

Sodium carbonate *Na_2CO_3*
Hydrocarbons from sulfonic acid hydrazides $NHNHSO_2R \rightarrow H$
s. *6*, 121

Sodium nitrite *$NaNO_2$*
Deamination of weak bases $NH_2 \rightarrow H$
s. *8*, 106

Cupric sulfate *$CuSO_4$*
Hydrocarbons from hydrazones $NHN{:}CR_2 \rightarrow H$
s. *8*, 107

Cupric sulfate/hypophosphorous acid *$CuSO_4/H_3PO_2$*
s. Hypophosphorous acid/cupric sulfate

Zinc *Zn*
Hydrocarbons from diazonium fluoborates $N_2^+ \rightarrow H$
s. *9*, 129

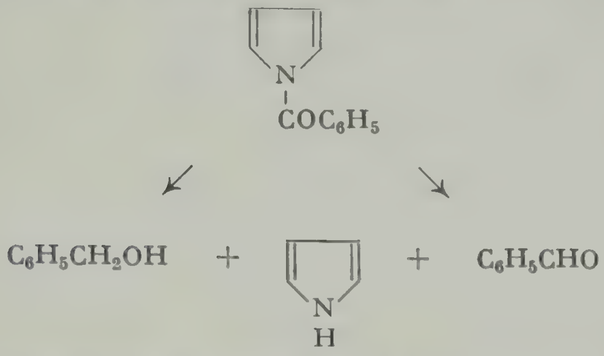
Zinc/acetic acid *Zn/CH_3COOH*
Tetracycline derivatives ←
Simultaneous elimination
of tert. amino and hydroxyl groups
s. *9*, 125

Lithium aluminum hydride *$LiAlH_4$*

Reduction of carboxylic acid amides by $LiAlH_4$ Hydroxymethyl compounds and aldehydes

$\mathrm{CON}\!<\begin{matrix}\nearrow \mathrm{CH_2OH}\\ \searrow \mathrm{CHO}\end{matrix}$

92.



Besides the usual reduction to amine (e. s. original), formation of alcohols and aldehydes may occur in certain cases.—E:

N-Benzoylpyrrole

reduced with 75% excess $LiAlH_4$ in ether, and the product isolated after 1 hr.'s heating → benzyl alcohol (Y: 80%) and pyrrole (Y: 85.6%).	reduced with 0.25 mole $LiAlH_4$ in ether by the reverse mode of addition at −10°, stirred 30 min. at −10° and 1 hr. at room temp. → benzaldehyde (Y: 54.1%) and pyrrole (Y: 82.1%).

F. e. s. V. M. Mićović and M. L. Mihailović, J. Org. Chem. *18*, 1190 (1953); aldehydes s. a. H. M. Walborsky, M. Baum, and D. F. Loncrini, Am. Soc. *77*, 3637 (1955).

s. *10*, 629

Aldehydes s. 8, 108

Mercaptans *RSH*

Hydrocarbons from tert. amines

$\mathrm{CH_2N}\!< \rightarrow \mathrm{CH_3}$

s. *10*, 484

Alkyl nitrite/irradiation ←

Replacement of amino groups by hydrogen

$\mathrm{NH_2} \rightarrow \mathrm{H}$

Photoreduction s. *9*, 126

Hypophosphorous acid *H_3PO_2*

s. 7, 117

Hypophosphorous acid/cupric sulfate *$H_3PO_2/CuSO_4$*

s. 7, 119

Sulfuric acid *H_2SO_4*

←

Aldehydes from 1-acyl-1,2-dihydroquinaldonitriles (Reissert compounds)

s. *6*, 122

Copper chromite *$CuCr_2O_4$*

Hydrocarbons from tert. amines $CH_2N\langle \rightarrow CH_3$

Hydrogenolysis of Mannich bases

s. *6*, 730

Hydrochloric acid *HCl*

Cleavage of azosulfonylthioethers N:NR → H

s. *9*, 140

Nickel *Ni*

Hydrogenolysis of Mannich bases $NR_2 \rightarrow H$

s. *9*, 127

Palladium-carbon *Pd-C*

Amines from diazo compounds ←

with simultaneous replacement

of halogen by hydrogen

s. *9*, 876

Platinum oxide *PtO_2*

Hydrogenolysis of unsatd. quaternary ammonium salts ←

s. *9*, 128

Via intermediates *v.i.*

Replacement of amino groups by hydrogen $NH_2 \rightarrow H$

via diazonium fluoborates

s. *9*, 129

Carboxylic acids from α-hydroxylactams C

via ketocarboxylic acids

s. *9*, 744

Halogen ↑ HC ⇅ Hal

Lithium hydride *LiH*

Replacement of chlorine by hydrogen Cl → H

s. *8*, 824

Sodium/liq. ammonia *Na/NH_3*

Stereospecificity

s. *7*, 738

Sodium iodide/acetic acid *NaI/CH_3COOH*

Replacement of halogen by hydrogen Hal → H

s. *9*, 130

Copper *Cu*

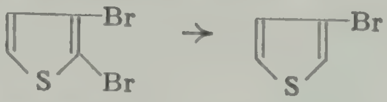
Replacement of chlorine by hydrogen Cl → H

s. *6*, 118

Magnesium *Mg*

Partial replacement of bromine by hydrogen Br → H

93.



An ethereal soln. of 2,3-dibromothiophene and ethyl bromide added during 45 min. to Mg, the reaction initiated with a crystal of iodine, refluxing continued 1.5-2 hrs., then hydrolyzed with ice and dil. HCl → 3-bromothiophene. Y: 78%. C. D. Hurd and K. L. Kreuz, Am. Soc. *74*, 2965 (1952); use of ethyl bromide as *activator* s. a. D. M. Bowen, Org. Synth., Coll. Vol. III, 553 (1955).

Replacement of halogen by deuterium Hal → D
s. *8*, 109

Zinc *Zn*

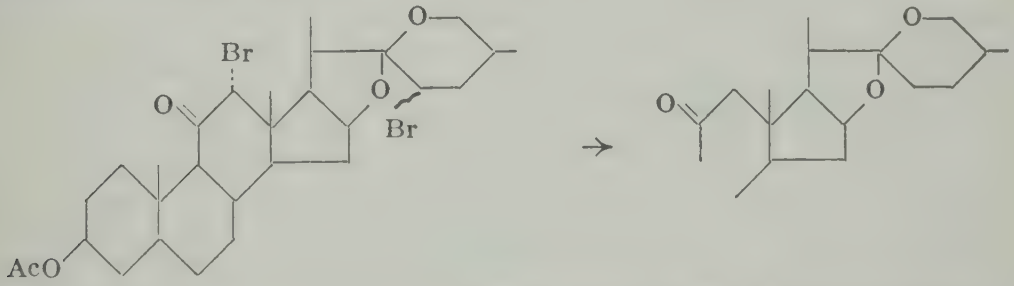
α,β-Ethyleneketones from α-halogen-α,β-ethyleneketones Hal → H
s. *8*, 110

Replacement of iodine by hydrogen I → H
s. *8*, 111

Zinc/sodium acetate/acetic acid *Zn/CH₃COONa/CH₃COOH*

Replacement of bromine by hydrogen Br → H

94.



500 mg. 12α,23ξ-dibromo-11-oxo-5α,22a-spirostan-3β-yl acetate added to a mixture of Zn-powder, annydrous Na-acetate, and acetic acid, then boiled 1 hr. → 350 mg. 11-oxo-5α,22a-spirostan-3β-yl acetate. J. W. Cornforth, J. M. Osbond, and G. H. Phillipps, Soc. *1954*, 907.

Zinc/cupric acetate/formamide *Zn/(CH₃COO)₂Cu/HCONH₂*

Hydrocarbons from 1,1,1-trichlorides with simultaneous replacement of trichloromethyl by amino groups ←
s. *8*, 113

Zinc/pyridine/acetic acid *Zn/C₅H₅N/CH₃COOH*

Hydrocarbons from 1,1-dichlorides $CCl_2 \rightarrow CH_2$
s. *8*, 114

Zinc/magnesium/hydrochloric acid *Zn/Mg/*

Selective replacement of iodine by hydrogen I →

95. $CF_3CH_2CI{=}CH_2 \rightarrow CF_3CH_2CH{=}CH_2$

4,4,4-Trifluoro-2-iodo-1-butene added to 25 g. Zn-powder, 2 g. Mg, a 50%-HCl, heated to 100° during 3 hrs. and the volatile product distill in vacuo → 4,4,4-trifluoro-1-butene. Y: 82%. R. N. Haszeldine, K. Le ham, and B. R. Steele, Soc. *1954*, 2040.

Zinc/acetic acid *Zn/CH₃CO*

Replacement of halogen by hydrogen Hal →
s. *9*, 108

Replacement of chlorine by hydrogen Cl →

Activated zinc
s. *9*, 131

Partial replacement
s. *7*, 120

Hydrocarbons and methyl ketones from trihalogenomethyl ketones
s. *8*, 115

Replacement of bromine by deuterium Br →
s. *8*, 116

Zinc/hydrochloric acid *Zn/H*

Selective replacement of iodine by hydrogen I →
s. *9*, 132

Zinc/hydrobromic acid *Zn/HB*

Replacement of halogen by hydrogen Hal →
s. *7*, 121

Zinc/nickel/ammonium chloride *Zn/Ni/NH₄*
s. Nickel/zinc/ammonium chloride

Zinc amalgam *Zn,H*

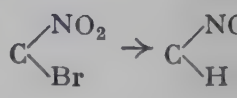
Hydrocarbons from trichloromethyl ketones $COCCl_3 \rightarrow CH_2CH$
s. *7*, 122

Mercury *H*

Reactions of radicals
Replacement of halogen by hydrogen Hal →
s. *7*, 123

Sodium boron hydride *NaBH*

Aliphatic nitro compounds from 1,1-nitrobromides
s. *9*, 168



Lithium aluminum hydride *LiAlH*

Replacement of halogen by hydrogen Hal →
s. *9*, 108

Prim. alcohols from carboxylic acid chlorides $COCl \rightarrow CH_2O$
s. *8*, 104

2-Ethylenealcohols from
α,β-ethylenecarboxylic acid chlorides
s. *9*, 133

1,5-Anhydroglycitols from acetohalogenosugars ←
s. *7*, 124

Lithium aluminum hydride/aluminum chloride $LiAlH_4/AlCl_3$
Halogenhydrins $COCl \rightarrow CH_2OH$
from halogenocarboxylic acid chlorides
s. *10*, 62

Lithium aluminum hydride/platinized asbestos ←
Phenanthridines from 9-chlorophenanthridines $Cl \rightarrow H$
s. *10*, 397

Lithium aluminum deuteride/lithium deuteride $LiAlD_4/LiD$
Replacement of halogen by deuterium $Hal \rightarrow D$
Optically active compounds s. *7*, 125

Aluminum chloride/lithium aluminum hydride $AlCl_3/LiAlH_4$
s. Lithium aluminum hydride/aluminum chloride

Ethyl alcohol C_2H_5OH
Disproportionation ←
s. *9*, 134

Stannous chloride/chromic acid $SnCl_2/CrO_3$
Elimination of substituents from 1,4-naphthoquinones ←
s. *10*, 99

Phosphorus/hydriodic acid P/HI
Replacement of chlorine by hydrogen $Cl \rightarrow H$
s. *6*, 120

Chromous chloride $CrCl_2$
Replacement of iodine by hydrogen $I \rightarrow H$
s. *7*, 901

Hydriodic acid HI
Replacement of chlorine by hydrogen $Cl \rightarrow H$
s. *9*, 135

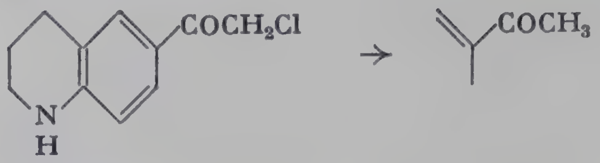
β-Diketones from α-bromo-β-diketones $Br \rightarrow H$
s. *8*, 117

Acoxy compounds from 1,1-acoxyhalides
Selective replacement of bromine by hydrogen
s. *7*, 126

Iron/hydrochloric acid *Fe/HCl*

Ketones from α-chloroketones Cl → H

96.



6-(Chloroacetyl)-1,2,3,4-tetrahydroquinoline in 80%-alcohol containing HCl heated with Fe-powder → 6-acetyl-1,2,3,4-tetrahydroquinoline. Y: 95%. H. de Diesbach et al., Helv. *35*, 2322 (1952); methods s. K. Matsumura, Am. Soc. *52*, 4433 (1930).

Nickel *Ni*

Replacement of chlorine by hydrogen
s. *1*, 93/4; *3*, 86; s. a. L. Pichat, C. Baret, and M. Audinot, Bl. *1954*, 88

Replacement of iodine by hydrogen I → H
s. *9*, 136

Replacement of bromine by deuterium Br → D
Deuterated steroids s. *7*, 127

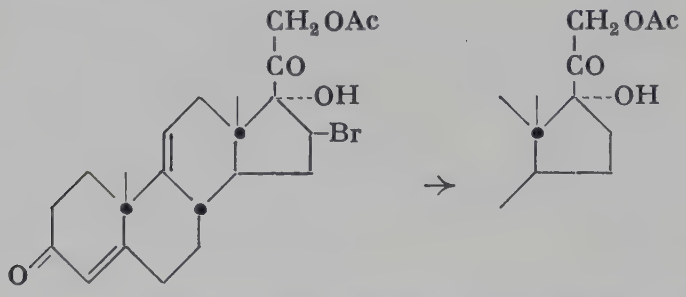
Nickel/zinc/ammonium chloride *Ni/Zn/NH₄Cl*

Replacement of chlorine by hydrogen Cl → H
s. *8*, 118

Nickel/acetic acid *Ni/CH₃COOH*

Replacement of halogen by hydrogen Hal → H

97.



Raney-Ni thoroughly washed with water until neutral, the water displaced with isopropanol, this slurry refluxed 1 hr. in acetone with stirring, then a little acetic acid, some water, and 3,20-diketo-16β-bromo-17α,21-dihydroxy-$\Delta^{4,9(11)}$-pregnadiene 21-acetate in acetone added, and refluxed an additional 4 hrs. → 3,20-diketo-17α,21-dihydroxy-$\Delta^{4,9(11)}$-pregnadiene 21-acetate. Y: 98%.—Similarly: 0.120 g. d,l-16β-bromocortisone acetate → 0.081 g. d,l-cortisone acetate. L. B. Barkley et al., Am. Soc. *76*, 5017 (1954).

Palladium *Pd*

Aldehydes from carboxylic acid chlorides COCl → CHO
s. *7*, 133

Palladium-calcium carbonate/pyridine $Pd\text{-}CaCO_3/C_5H_5N$

Hydrocarbons from α,β-ethylenechlorides $C{:}CCl \rightarrow CHCH_2$
Selective hydrogenation
s. *9*, 137

Palladium-strontium carbonate $Pd\text{-}SrCO_3$

Replacement of halogen by hydrogen Hal → H
s. *7*, 128

Palladium-barium sulfate $Pd\text{-}BaSO_4$
s. *8*, 84

simultaneously amines from nitro compounds
s. *6*, 35

Selective replacement of chlorine by hydrogen Cl → H
with subsequent replacement of chlorine by hydroxyl
s. *8*, 252

Replacement of chlorine by hydrogen,
also with simultaneous formation
of lactones from ketocarboxylic acids
s. *8*, 119

Palladium-barium sulfate/dimethylaniline $Pd\text{-}BaSO_4/C_6H_5N(CH_3)_2$

Replacement of chlorine by hydrogen
s. *7*, 129

Palladium/barium sulfate/calcium carbonate $Pd\text{-}BaSO_4/CaCO_3$

Replacement of bromine by hydrogen Br → H
s. *9*, 138

Palladium-carbon $Pd\text{-}C$

Replacement of halogen by hydrogen Hal → H
s. *6*, 731

with hydrogenation of a carbon-carbon double bond
s. *7*, 87

simultaneously: amines from diazo compounds
s. *9*, 876

Replacement of chlorine by hydrogen Cl → H
s. *4*, 113; purines s. A. Bendich, P. J. Russell, Jr., and J. J. Fox, Am. Soc. *76*, 6073 (1954)

Replacement of bromine by hydrogen Br → H
Tropolones s. *7*, 130

Palladium-carbon/ammonia $Pd\text{-}C/NH_3$

Replacement of chlorine by hydrogen Cl → H
s. *7*, 131

Palladium-carbon/magnesium oxide $Pd\text{-}C/MgO$
s. *8*, 120; s. a. C. G. Overberger and J. C. Kogon, Am. Soc. *76*, 1879 (1954)

Palladium-carbon/calcium oxide *Pd-C/CaO*
s. *7*, 132

Via intermediates *v.i.*

Replacement of chlorine by hydrogen via sulfonic acid hydrazides $Cl \rightarrow H$
s. *6*, 121

Prim. alcohols from carboxylic acid chlorides via aldehydes $COCl \rightarrow CHO \rightarrow CH_2OH$
s. *7*, 133

Alcohols from halogenhydrins via oxido compounds ←
Optically active compounds s. *7*, 579

Aldehydes from carboxylic acid chlorides via 1-acyl-1,2-dihydroquinaldonitriles (Reissert compounds) $COCl \rightarrow CHO$
s. *6*, 122

Sulfur ↑ HC⇵S

Sodium amalgam *Na,Hg*

Reductive cleavage of sulfones to hydrocarbons and sulfinic acids $RSO_2R' \rightarrow RH + HSO_2R'$
s. *9*, 139

Sodium hydroxide *NaOH*

Cleavage of ketothioethers ←
s. *8*, 121

Sodium/liq. ammonia *Na/NH₃*

Reductive cleavage of sulfones $RSO_2R' \rightarrow RH$
Reactions of 1,1-disulfones

98. $(n\text{–}C_4H_9)_2C(SO_2C_2H_5)_2 \rightarrow (n\text{–}C_4H_9)_2CHSO_2C_2H_5$

Na added in small pieces to a suspension of 5,5-bis(ethylsulfonyl)-nonane in liq. NH_3 until the soln. becomes blue, then allowed to stand for 1 hr. → 5-ethylsulfonylnonane. Y: 86%. F. e. and reactions s. M. W. Cronyn and E. Zavarin, J. Org. Chem. *19*, 139 (1954).

Diethylamine $(C_2H_5)_2NH$

Replacement of alkylthio groups by hydrogen $RSR' \rightarrow RH$
Cleavage of sulfonylthioethers
s. *7*, 310

Piperidine $C_5H_{11}N$

Cleavage of azosulfonylthioethers
s. *9*, 140

Cleavage of sulfonylnitro compounds ←
s. *9*, 141

Zinc amalgam *Zn,Hg*

Ketones from ketothioethers ←

s. *9*, 142

Mercuric sulfate *$HgSO_4$*

Desulfonation $SO_3H \rightarrow H$

s. *8*, 122

Lithium aluminum hydride *$LiAlH_4$*

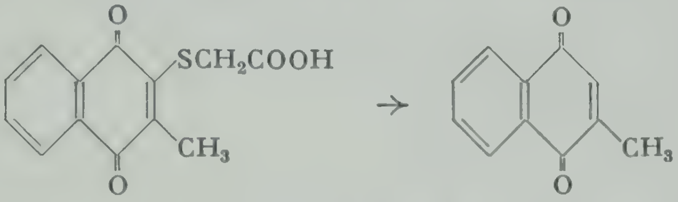
Methylamines from isothiocyanates N:C:S → $NHCH_3$

s. *9*, 143

Stannous chloride/chromic acid *$SnCl_2/CrO_3$*

Elimination of substituents from 1,4-naphthoquinones ←

9.



The groups Hal, NHC_6H_5, SR, SO_2R, SO_3H, and (in some cases) OH can be removed from positions 2 and 3 of 1,4-naphthoquinones by refluxing with $SnCl_2$-HCl-acetic acid and subsequent reoxidation of the dil. reaction liquor with CrO_3.—E: 3-Carboxymethylthio-2-methylnaphthoquinone → 2-methylnaphthoquinone. Y: 90%. F. e. s. D. B. Bruce and R. H. Thomson, Soc. *1954*, 1428.

Sulfuric acid *H_2SO_4*

Desulfonation $SO_3H \rightarrow H$

s. *7*, 478; *9*, 306

Hydrochloric acid *HCl*

Partial desulfonation

s. *7*, 134

Nickel *Ni*

Replacement of alkylthio groups by hydrogen RSR′ → RH

s. *9*, 145

Hydrocarbons from thioethers

s. *9*, 144

Replacement in pyrimidines,
simultaneously: amines from nitro compounds

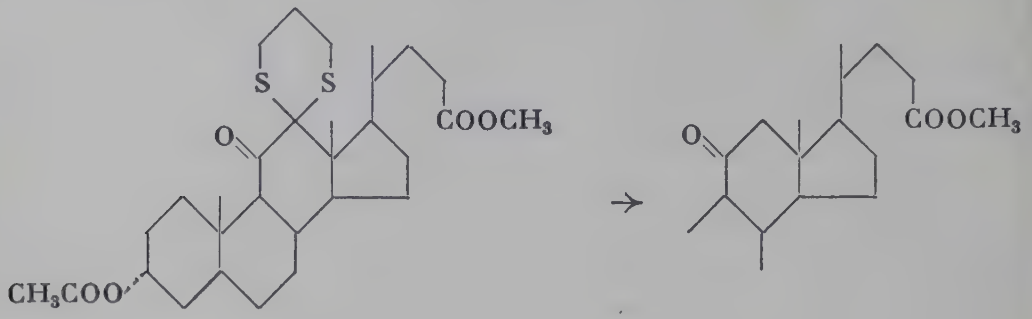
s. *8*, 123

Desulfuration of thioenolethers C:C(SR) → C:CH

Deactivated catalyst s. *6*, 123

Hydrocarbons from mercaptals $C(SR)_2 \rightarrow CH_2$
s. *7*, 116, 627

100.



from cyclic mercaptals. A suspension of methyl 3α-acetoxy-11,12-diketocholanate-12-trimethylenethioketal in methanol containing wet Raney-Ni catalyst shaken for 6 hrs. → methyl 3α-acetoxy-11-ketocholanate. Y: 95%. S. Archer et al., Am. Soc. *76*, 4915 (1954).

Hydrocarbons from thiocyanates SCN → H
s. *7*, 621

Amines from carboxylic acid thioamides
Cyclic amines from thiolactams
N-Alkylation $CSN\langle \rightarrow CH_2N\langle$
s. *6*, 124

Phenanthridines from phenanthrithiones
s. *9*, 574

Hydrocarbons from sulfones and thioethers ←
Stereochemistry of reductive desulfuration
s. *9*, 145

Hydrocarbons from 1,1-disulfones $C(SO_2R)_2 \rightarrow CH_2$
s. *9*, 880

Lactones from carbalkoxythiolic acid esters ○
s. *7*, 135

Ring opening by desulfuration ↺

Thiophene ring opening
s. *9*, 146; chain-lengthening cf. G. M. Badger, H. I. Rodda, and W. H. F. Sasse, Chem. and Ind. *1954*, 308; T. F. Grey et al., Chem. and Ind. *1954*, 578

Thiazole ring opening
s. *8*, 124

Phenothiazine ring opening
s. *7*, 136

1,2,4-Thiadiazine ring opening
s. *6*, 125

Alkaline nickel

←

Hydrocarbons from thioethers
with simultaneous cleavage of acetals
s. *7*, 137

RSR′ → RH

Nickel/sodium carbonate *Ni/Na_2CO_3*

Carboxymethyl thioethers as intermediates
s. *6*, 482

Nickel/aluminum *Ni/Al*

↺

Reductions of sulfur compounds
with nickel aluminum alloy
Thianaphthene ring opening
s. *6*, 126

Remaining Elements ↑ HC⇅Rem

Sodium/alcohol or potassium hydroxide/alcohol *NaOR or KOH/C_2H_5OH*

Cleavage of silanes ←
s. *9*, 147

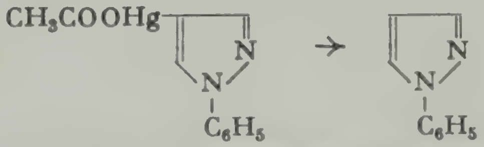
Lithium/liq. ammonia or sodium/liq. ammonia *Li/NH_3 or Na/NH_3*

Arenes from phosphoric acid aryl esters $ArOPO(OR)_2 \rightarrow ArH$
s. *10*, 107

Hydrochloric acid *HCl*

Cleavage of organomercury compounds ←

101.



4-Acetoxymercuri-1-phenylpyrazole distilled with dil. HCl → 1-phenylpyrazole. Y: 80%. F. e. s. I. L. Finar and K. E. Godfrey, Soc. *1954*, 2293.

Cleavage of silanes ←
s. *7*, 138

Nickel *Ni*

Deselenization ←
s. *9*, 148

Carbon ↑ HC⇅C

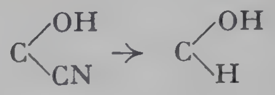
Without additional reagents *w.a.r.*

Reverse Mannich reaction $CH_2NR_2 \rightarrow H$
s. *7*, 139

Reductive cleavage of dimers $R{\cdot}R \rightarrow 2RH$
s. *8*, 128

Sodium *Na*

Replacement of cyano groups by hydrogen
Sec. alcohols from cyanohydrins



$$C(OH)(CN) \rightarrow C(OH)(H)$$

s. *8*, 725; replacement of cyano groups by hydrogen s. a. L. A. Walter and S. M. McElvain, Am. Soc. *56*, 1614 (1934)

Sodium hydroxide *NaOH*

Ketones from α-aminomethyleneketones $C{:}CHNR_2 \rightarrow CH_2$
Blocking of ketone α-positions
s. *2*, 725a; s. a. P. B. Talukdar and P. Bagchi, J. Org. Chem. *20*, 13 (1955)

Replacement of C-acyl by hydrogen $COR \rightarrow H$
s. *9*, 149

Replacement of carbalkoxy groups by hydrogen $COOR \rightarrow H$
s. *8*, 844; *10*, 5

  Ketones from β-ketocarboxylic acid esters
  s. *9*, 150

  Replacement at low temp.
  s. *9*, 151

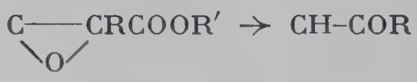
Methyl ketones $C{\vdots}C\cdot COOH \rightarrow COCH_3$
from α,β-acetylenecarboxylic acids
s. *7*, 906

Subst. glutaric acids ←
from arylmethylene-bis-acetoacetates
s. *6*, 759

α-Aminocarboxylic acids ←
from α-formamidomalonic esters
s. *6*, 127, 789; neutralization with HCl instead of acetic acid s. A. Ek and B. Witkop, Am. Soc. *76*, 5579 (1954)

Sodium hydroxide/alcohol

Ketones from glycidic acid esters
s. *6*, 129



$$C{-}CRCOOR' \rightarrow CH{-}COR$$

Potassium hydroxide *KOH*

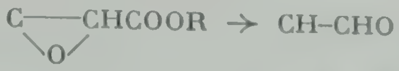
Ketones from α-aminomethyleneketones $C{:}CHNR_2 \rightarrow CH_2$
Blocking of ketone α-positions
s. *9*, 769

Replacement of carbalkoxy groups by hydrogen $COOR \rightarrow H$
s. *8*, 125

  γ-Diketones from β,γ′-diketocarboxylic acid esters
  s. *9*, 892

α-Acylaminocarboxylic acids from α-acylaminomalonic acid esters
s. *9*, 152

Aldehydes from glycidic acid esters
s. *8*, 842


$\underset{\diagdown O \diagup}{C\text{—}CHCOOR} \rightarrow CH\text{–}CHO$

Replacement of cyano groups by hydrogen CN → H
s. *10*, 620

Carboxylic acids from cyanocarboxylic acid esters
s. *6*, 700

γ-Pyrone ring opening C
s. *6*, 128

Potassium hydroxide/alcohol

Lactols from acoxyketones ○
s. *8*, 126

Sodium/alcohol *NaOR*

α-Iodoketones from β-iodo-α,γ-diketocarboxylic acid esters COCOOR → H
s. *10*, 162

Reverse Mannich reaction CH_2NR_2 → H
s. *7*, 140

Sodium carbonate *Na_2CO_3*

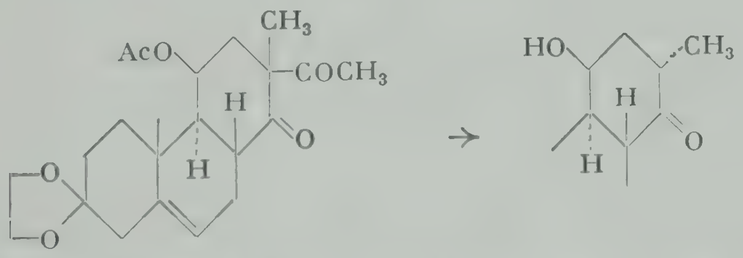
Ketones from β-ketocarboxylic acid esters COOR → H
s. 7, 141; γ-acetyleneketones s. J. Colonge and R. Gelin, Bl. *1954*, 208

α-Acetamidocarboxylic acids from acetamidomalonic esters and -α-cyanocarboxylic esters ←
s. *6*, 130

Potassium carbonate *K_2CO_3*

Replacement of C-acyl by hydrogen with simultaneous deacetylation COR → H

2.



A soln. of 2,4b-dimethyl-2-acetyl-7-ethylenedioxy-1.2.3.4,4aα,4b,5,6,7.8.-10,10aβ-dodecahydrophenanthrene-4β-ol-1-one acetate and K-carbonate in aq. 50%-methanol refluxed 16 hrs. → 2α.4b-dimethyl-7-ethylenedioxy-1.2,3,4,4aα,4b.5,6.7,8,10.10aβ-dodecahydrophenanthren-4β-ol-1-one. Y: 76%. R. M. Lukes et al., Am. Soc. 75, 1707 (1953).

Ammonia *NH_3*

Carboxylic acids from barbituric acids C
s. *6*, 228

Magnesium oxide/cupric acetate $MgO/(CH_3COO)_2Cu$

β-Ketocarboxylic acid esters from acylmalonic acid esters ←

s. *7*, 142

Calcium oxide *CaO*

Hydrocarbons from dicarboxylic acid anhydrides ←

s. *8*, 127

Benzo[mno]fluoranthenes

s. *9*, 153

Barium hydroxide/copper $Ba(OH)_2/Cu$

s. *7*, 143

Zinc amalgam *Zn,Hg*

Hydrocarbons from β-ketocarboxylic acid esters by Clemmensen reduction ←

s. *9*, 154

Phenylmagnesium bromide C_6H_5MgBr

Reductive cleavage of dimers R·R → 2 RH

s. *8*, 128

Aluminum amalgam *Al,Hg*

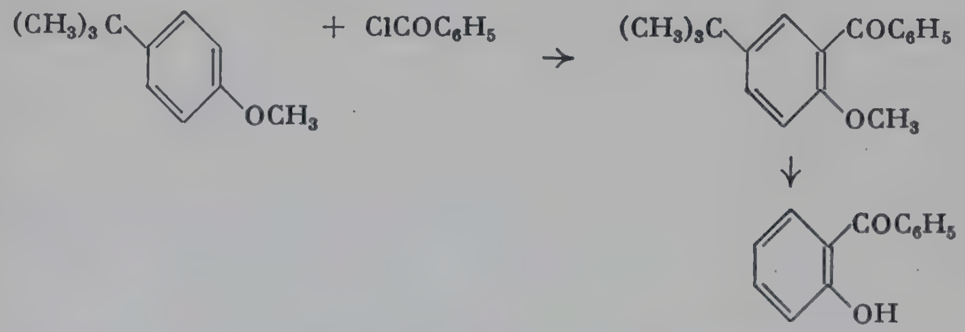
Reductive cleavage of pyrimido[4,5-b]pyrazine side chains ←

s. *9*, 155

Aluminum chloride $AlCl_3$

tert-Butyl as C-blocking group
Ketones from carboxylic acid chlorides
Removal of the blocking group with simultaneous ether cleavage $ArC(CH_3)_3 \rightarrow ArH$
o-Hydroxybenzophenones

103.



A soln. of p-*tert*-butylanisole, benzoyl chloride, *sym*-tetrachloroethane, and $ZnCl_2$ refluxed 40 hrs. → 2-methoxy-5-*tert*-butylbenzophenone (Y: 66%) in dry benzene treated with 4 moles of $AlCl_3$, and heated 45 hrs. at 65-70° → 2-hydroxybenzophenone (Y: 79%). F. e. s. M. Kulka, Am. Soc. *76*, 5469 (1954).

Nitrobenzene $C_6H_5NO_2$
Aldehydes by oxydative degradation of side-chains COR → CHO
s. *7*, 321

Acetic acid CH_3COOH
Synthesis of ketones COOR → H
with 2-tetrahydropyranyl malonates
Replacement of carbalkoxy groups by hydrogen
s. *8*, 839

Silica-zirconia-alumina $SiO_2/ZrO_2/Al_2O_3$
Dealkylation of alkylbenzenes ArR → ArH
Depropylation s. *7*, 144

Phosphoric acid H_3PO_4
Hydrocarbons from carboxylic acid amides $CONH_2$ → H
s. *7*, 145

Polyphosphoric acid $H(PO_3H)_xOH$
Replacement of cyano groups by hydrogen CN → H
s. *9*, 156

Hydrogen peroxide H_2O_2
Benzopyran ring opening ⊂
s. *8*, 129

Hydrosulfite $S_2O_4^{--}$
Reductive cleavage R·R → 2 RH
s. *7*, 146

p-Toluenesulfonic acid TsOH
Replacement of carbalkoxy groups by hydrogen COOR → H
  tert-Butyl esters as intermediates
  s. *3*, 703; *9*, 881

Sulfuric acid H_2SO_4
  Sulfonylacetic acid esters
  from sulfonylmalonic acid esters
  s. *9*, 669

Hydrocarbons $CH(COCH_3)COOR$ → CH_3
from β-ketocarboxylic acid esters
s. *6*, 131
  Methyl ketones from
  β,β-diketocarboxylic acid esters
  s. *6*, 133

Hydrocarbons from malonic acid esters $CH(COOR)_2$ → CH_3
s. *6*, 132
  Methyl ketones from acylmalonic acid esters
  s. *6*, 285

Replacement of cyano groups by hydrogen CN → H
s. *8*, 130; ketones from α-cyanoketones s. S. B. Coan and E. I. Becker, Org. Synth. *35*, 32 (1955)

Carboxylic acids from cyanocarboxylic acid esters
s. *7*, 158

Sym. ketones from ketene dimers ←
s. *7*, 862

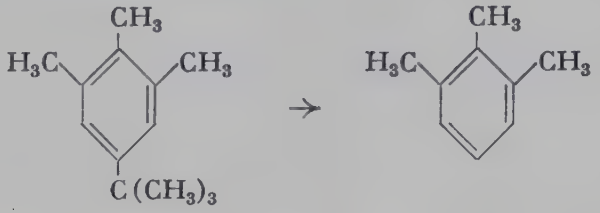
Copper chromite *$CuCr_2O_4$*

Hydrogenolysis of the carbon-carbon bond CROH → CHOH
s. *6*, 134

Hydrofluoric acid *HF*

tert-Butyl as C-blocking group $ArC(CH_3)_3$ → ArH
Removal of the blocking group

104.

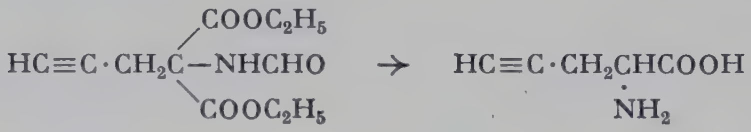


The *tert*-butyl group is an unusual removable blocking group because it blocks not only the position it occupies, but the two adjacent positions as well. As a substituent on ar. nuclei it increases the ease of further substitution in the *meta* and particularly in the *para* positions. It can be removed readily from ar. hydrocarbons without disturbing the remaining alkyl groups.—E: A mixture of 1,2,3-trimethyl-5-*tert*-butylbenzene, m-xylene, and liq. anhydrous HF stirred vigorously in a copper flask immersed in an ice bath for 4.5 hrs. → 1,2,3-trimethylbenzene. Y: 77%; 96% based on startg. m. consumed. F. e. s. M. J. Schlatter, Am. Soc. *76*, 4952 (1954).

Hydrochloric acid *HCl*

α-Aminocarboxylic acids from formamidomalonic esters ←
Acetylene-α-aminocarboxylic acids

105.



$$HC{\equiv}C{\cdot}CH_2C(COOC_2H_5)_2{-}NHCHO \rightarrow HC{\equiv}C{\cdot}CH_2CH(NH_2)COOH$$

A mixture of diethyl propargylformamidomalonate and 10%-HCl gently refluxed for 4 hrs. → propargylglycine. Y: 85%.—Hydrolysis with dil. H_2SO_4 has a tendency to hydrate the triple bond, while HBr-hydrolysis results in the addition of HBr. H. Gershon et al., Am. Soc. *76*, 3484 (1954).

α-Amino-γ-dicarboxylic acids ←
s. *10*, 576; s. a. D. C. Morrison, Am. Soc. *77*, 6072 (1955)

Dicarboxylic acids from dicyanocarboxylic acid esters ←
s. *6*, 705

β-Subst. glutaric acids from α,α′-dicyanoglutaramides ←
s. *10*, 577

Hydroxyketones from ketolactones C
s. *7*, 147

Hydriodic acid *HI*

α-Aminocarboxylic acids ←
from acylaminomalonic acid esters
with simultaneous cleavage of ethers
s. *9*, 157

Palladium-carbon *Pd-C*

Reductive 2,4-oxazolidione ring opening C
s. *9*, 158

Via intermediates *v.i.*

Replacement of methyl groups by hydrogen $CH_3 \rightarrow H$
s. *6*, 135

Hydrolysis and decarboxylation $COOR \rightarrow H$
s. *6*, 136; *9*, 122, 159, 884

α-Acylaminocarboxylic acids
from acylaminomalonic acid esters
Selective Hydrolysis
s. *6*, 137

Elimination

Oxygen ↑ HC ⇑ O

Sodium/liq. ammonia *Na/NH₃*

Hydrocarbons from α,β-ethylenealcohols ←
s. *6*, 138

Zinc *Zn*

Hydrocarbons from phenols $OH \rightarrow H$
s. *8*, 131

Zinc/Ammonia *Zn/NH₃*
s. *10*, 537

Zinc/copper sulfate/alkali hydroxide ←

Anthracenes from anthrones ←
s. *6*, 139

Zinc/acetic acid *Zn/CH_3COOH*

Hydrocarbons from hydroxy compounds OH → H
s. *7*, 148

Zinc amalgam *Zn,Hg*

Hydrocarbons from tert. alcohols
s. *7*, 149; with Zn, Hg and Zn-dust s. N. Campbell, A. Marks, and G. V. McHattie, Soc. *1955*, 1190

Ketones from acyloins
s. *8*, 132

Lithium aluminum hydride *$LiAlH_4$*

Aldehydes from carboxylic acids COOH → CHO
s. *9*, 112

Hydroxyketones from ketocarboxylic acid esters ←
Protection of keto groups

  by formation of ketals
  s. *8*, 133

  by formation of enolethers
  with simultaneous migration
  of a carbon-carbon double bond
  s. *7*, 150

Imidazolones from hydantoins ←
Selective reduction
s. *7*, 151

Formic acid/sodium carbonate *$HCOOH/Na_2CO_3$*

Hydrocarbons from hydroxy compounds OH → H
s. *7*, 152

Tin/copper sulfate and stannous chloride *$Sn/CuSO_4$ and $SnCl_2$*

Desoxybenzoins from benzoins
s. *7*, 153

Stannous chloride *$SnCl_2$*

Carboxylic acid esters
from α-hydroxycarboxylic acid esters
s. *8*, 720

Hydrogen sulfide *H_2S*

Reduction of pyrimidines ←
s. *8*, 134

Copper chromite *$CuCr_2O_4$*

Hydrocarbons from alcohols OH → H
s. *6*, 107

Tungsten disulfide *WS_2*

Hydrocarbons from alcohols, ketones, carboxylic acid esters and anhydrides ←

06. $(C_3H_7)_2CHOH \rightarrow (C_3H_7)_2CH_2$

Tungsten disulfide is an excellent catalyst for the hydrogenolysis of oxygen-containing compounds.—E: Crude 4-heptanol hydrogenated with WS_2 at 340° and an initial pressure of 105 atm. → n-heptane. Y: 93%. F. e. s. S. Landa and J. Mostecký, Coll. Czech. Chem. Communs. *20*, 430 (1955).

Hydriodic acid *HI*

s. *8*, 99

Carboxylic acids from hydroxycarboxylic acid esters ←
Reductive hydrolysis
s. *7*, 699

Hydriodic acid/acetic anhydride *$HI/(CH_3CO)_2O$*

Hydrocarbons from diols OH → H
s. *9*, 160

Nickel *Ni*

Hydrocarbons from phenols
s. *6*, 140

Platinum oxide *PtO_2*

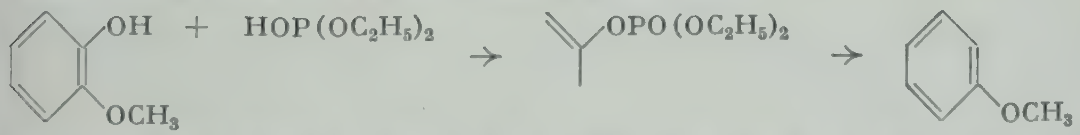
Replacement of hydroxyl by hydrogen
s. *6*, 112

Via intermediates *v.i.*

Hydrocarbons from alcohols via halides
s. *9*, 108

Replacement of hydroxyl by hydrogen via bromides
s. *6*, 141

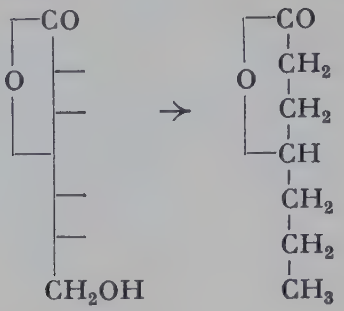
Arenes from phenols via phosphoric acid aryl esters
Phosphoric acid esters from dialkyl phosphites



Triethylamine added slowly with vigorous shaking to an ice-cooled soln. of pyrocatechol monomethyl ether in CCl_4 and diethyl phosphite, allowed to stand overnight at room temp. → o-methoxyphenyl diethyl phosphate (Y: 85%) dissolved in liq. NH_3, exactly 2 equivalents of Na or Li added in small pieces with shaking during ca. 5 min. → anisole (Y: 90% with Na, 88% with Li).—The reaction is much less successful with dihydric phenols. F. method for the prepn. of the phosphates s. G. W. Kenner and N. R. Williams, Soc. *1955*, 522.

Lactones from hydroxylactones
Modified Kiliani reduction

108.



α-Glucoheptonic lactone refluxed with *HI* (D. 1.7) and red *P* for 2 hrs. and the crude product deiodinated by dissolving in 2 *N* NaOH treating cautiously with *Ni-Al-alloy* during 10 min., and heating 75 min. at 90-95° with occasional stirring after foaming has subsided → heptonic lactone. Crude Y: 70-72%.—Kiliani's original procedure gives n-heptanoic acid in variable yields. By shortening the reaction time, the above lactone is obtained in good yield. Also reduction of Na-salts s. A. S. Perlin and C. B. Purves, Can. J. Chem. *31*, 227 (1953).

Sulfur ↑

HC ⇑ S

Nitric acid/nitrous acid HNO_3/HNO_2

Replacement of sulfhydryl by hydrogen SH → H

s. *6*, 142

Ferric chloride $FeCl_3$

Imidazoles from 2-mercaptoimidazoles

s. *8*, 401

Nickel *Ni*

s. *7*, 154; pyrimidine derivatives s. H. M. Foster and H. R. Snyder, Org. Synth. *35*, 80 (1955)

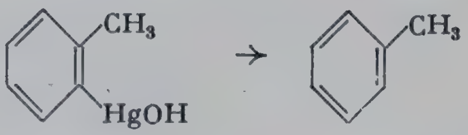
Remaining Elements ↑

HC ⇑ Rem

Irradiation ←

Hydrocarbons from organomercuric hydroxides HgOH → H

109.



o-Tolylmercuric hydroxide in Ethyl Cellosolve UV-irradiated for 18 hrs. → toluene. Y. 82.6%. F. e. s. G. A. Razuvaev and G. G. Petukhov, Ж. *23*, 37 (1953); C. A. *48*, 622c.

Carbon ↓

HC ⇑ C

Without additional reagents

w.a.r.

Decarboxylation COOH → H
s. *6*, 135, 137; *8*, 741; *9*, 159

by azeotropic distillation
s. *9*, 122

α-Chlorocarboxylic acids from α-chloro-α-dicarboxylic acids
s. *7*, 570

β,γ-Ethylenenitriles from α,β-ethylene-α-cyanocarboxylic acids
s. *7*, 796

Double decarboxylation
s. *7*, 827

Sodium hydroxide *NaOH*

Deformylation CHO → H
s. *10*, 619

Potassium hydroxide *KOH*

Phthalides ←
s. *9*, 161

Deformylation with simultaneous formation of cyclic α,β-ethyleneketones from diketones CHO → H
s. *7*, 872

Decarboxylation COOH → H
s. *7*, 155

Sodium/alcohol *NaOR*

Deformylation CHO → H
s. *7*, 743

Sodium salt Na^+

Decarboxylation COOH → H
s. *8*, 944

Dimethylaniline $C_6H_5N(CH_3)_2$

s. *6*, 136

Pyridine C_5H_5N

s. *7*, 156

Copper-nickel *Cu-Ni*

Dehydroxymethylation CH_2OH → H
s. *9*, 162

Cupric sulfate/quinoline ←

Decarboxylation COOH → H

s. *7*, 157

Replacement of carboxyl by deuterium via carboxylic acid chlorides

s. *8*, 134a

Calcium hydroxide $Ca(OH)_2$

s. *6*, 796

Dimethylformamide $HCON(CH_3)_2$

s. *9*, 163

Enzyme ←

s. *9*, 164

Resorcinol ←

s. *6*, 143

Acetic acid CH_3COOH

Partial decarboxylation

s. *7*, 158

Sulfuric acid H_2SO_4

Deformylation CHO → H

s. *6*, 144

Selenium dioxide SeO_2

Elimination of side chains CH_3 → H

s. *8*, 310

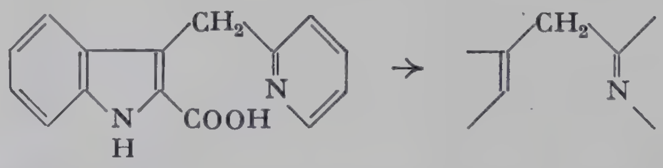
Copper chromite/quinoline ←

Decarboxylation COOH → H

s. *1*, 112; *2*, 124/5; s. a. H. N. Rydon and J. C. Tweddle, Soc. *1955*, 3499; steroids s. F. Sondheimer et al., Am. Soc. *77*, 4145 (1955)

Hydrochloric acid HCl

110.



6 g. 3-(2-pyridylmethyl)indole-2-carboxylic acid boiled 1 hr. with concd. HCl → 4.1 g. 3-(2-pyridylmethyl)indole. G. R. Clemo and J. C. Seaton, Soc. *1954*, 2582.

4-Pyrones ←

s. *8*, 135

Nickel-copper s. Copper-nickel *Ni-Cu*

Nickel-silica $Ni\text{-}SiO_2$

Dehydroxymethylation CH_2OH → H

s. *6*, 145

Formation of O—O Bond

Uptake

Addition to Hydrogen and Oxygen OO ⇓ HO

Sulfuric acid *H_2SO_4*

Hydroperoxides from alcohols OH → OOH
Acetylene hydroperoxides
s. *7*, 159

Peroxycarboxylic acids from carboxylic acids COOH → CO_2H

11. $CH_3[CH_2]_{10}COOH \rightarrow CH_3[CH_2]_{10}COO_2H$

50% excess of 50%-H_2O_2 added dropwise during 10 min. to a soln. of lauric acid in 95%-H_2SO_4 at such a rate that the temp. is kept between 20 and 30°, stirring continued for 50 min. → perlauric acid. Purity: 97%. Conversion: ca. 100%. F. e., also from esters, s. W. E. Parker et al., Am. Soc. 77, 4037 (1955).

Addition to Oxygen and Carbon OO ⇓ OC

Sodium hydroxide *NaOH*

Acyl peroxides ·CO·O·OC· → ·CO·OO·OC·
from carboxylic acid anhydrides
s. *9*, 165

Exchange

Sulfur ↑ OO ⇅ S

Potassium hydroxide *KOH*

Hydroperoxides from methylsulfonates $\cdot OSO_2CH_3 \rightarrow \cdot OOH$
s. *9*, 166

Formation of O—N Bond

Uptake

Addition to Nitrogen ON⇓N

Peracetic acid *CH_3COO_2H*

Formation and reduction of N-oxides ←
Deoxygenation in the presence of oxidizing agents
s. *8*, 136

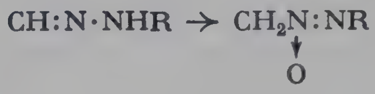
Trifluoroperacetic acid CF_3COO_2H

N-Nitramines from N-nitrosamines $N{\cdot}NO \rightarrow N{\cdot}NO_2$
s. *9*, 169

Perphthalic acid ←

N-Oxides as intermediates $N\rightarrow O$
s. *6*, 389

Azoxy compounds from hydrazones and reverse reaction
s. *9*, 167



$CH{:}N{\cdot}NHR \rightarrow CH_2\underset{\substack{\downarrow\\ O}}{N}{:}NR$

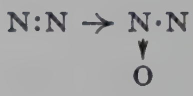
Nitrogen dioxide NO_2

Hydroxyhydrazines from hydrazyl radicals $N{\cdot}N(OH)$
s. *9*, 988

Nitric acid HNO_3

Aliphatic nitro compounds from oximes via 1,1-nitrosobromides and 1,1-nitrobromides $NO \rightarrow NO_2$
s. *9*, 168

Azoxy from azo compounds
s. *8*, 137



$N{:}N \rightarrow \underset{\substack{\downarrow\\ O}}{N}{\cdot}N$

Hydrogen peroxide H_2O_2

N-Oxides $N\rightarrow O$
s. *9*, 243; *10*, 671

Exchange

Hydrogen ↑ **ON⇅H**

Potassium salt K^+

O-Azo compounds $\cdot ON{:}NR$
s. *9*, 419

Copper(I,II) sulfite ←

Nitro compounds from amines $NH_2 \rightarrow NO_2$
s. *5*, 97; s. a. E. R. Ward and T. M. Coulson, Soc. *1954*, 4545; H. Singer and W. Shive, Am. Soc. *77*, 5700 (1955)

Trifluoroperacetic acid CF_3COO_2H

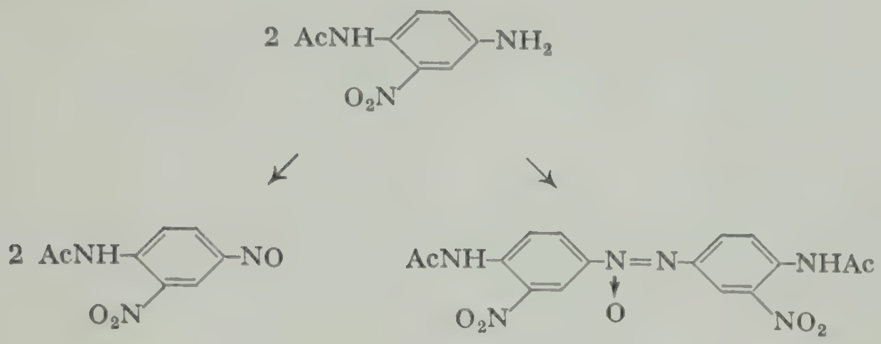
Oxidations with trifluoroperacetic acid
s. *9*, 169

Hydrogen peroxide/sulfuric acid H_2O_2/H_2SO_4
s. *7*, 160

Peroxymonosulfuric acid *H_2SO_5*

Nitroso and azoxy compounds from amines ←

12.



A slightly warm, supersatd. soln. of 4-amino-2-nitroacetanilide in dioxane added quickly to *neutralized* Caro's acid soln., and the mixture shaken for 10 min. → 2-nitro-4-nitrosoacetanilide. Y: 56%.

A hot aq. soln. of 4-amino-2-nitroacetanilide added to Caro's acid soln. containing ice, and allowed to stand for 16 hrs. → 4,4'-diacetamido-3,3'-dinitroazoxybenzene. Y: 50%.

C. M. Atkinson et al., Soc. *1954*, 2023.

Potassium permanganate *$KMnO_4$*

tert-Nitroparaffins from tert-carbinamines $NH_2 \rightarrow NO_2$

3. $(CH_3)_3C{\cdot}NH_2 \rightarrow (CH_3)_3C{\cdot}NO_2$

tert-Butylamine added during 15 min. to a stirred mixture of K-permanganate and water, stirred 8 hrs., then kept 8 hrs. at ca. 55° → *tert*-nitrobutane. Y: 83%. F. e. s. N. Kornblum and R. J. Clutter, Am. Soc. *76*, 4494 (1954).

Oxygen ↑ ON⇅O

Without additional reagents *w.a.r.*

Nitric acid esters ONO_2

s. *8*, 416

Acetic anhydride *$(CH_3CO)_2O$*

s. *3*, 101; also cyanohydrin nitrates s. W. D. Emmons and J. P. Freeman, Am. Soc. *77*, 4387 (1955)

Phosphorus pentoxide P_2O_5

s. *8*, 138

Elimination

Hydrogen ↑ ON⇑H

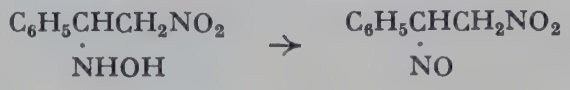
Phenyl iodosoacetate *$C_6H_5I(OAc)_2$*

Benzofurazan oxides from o-nitramines ○
s. *9*, 385

Chromic acid *CrO_3*

Pseudonitrosites from 2-nitrohydroxylamines NHOH → NO

114.



$$\underset{NHOH}{C_6H_5\dot{C}HCH_2NO_2} \rightarrow \underset{NO}{C_6H_5\dot{C}HCH_2NO_2}$$

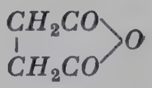
Aq. Na-dichromate added below 0° to a soln. of 9.1 g. N-(1-phenyl-2-nitroethyl)hydroxylamine (prepn. s. 276) in H_2SO_4-water → 7.0 g. crude styrene pseudonitrosite. C. D. Hurd and J. Patterson, Am. Soc. *75*, 285 (1953).

Oxygen ↑ ON⇑O

Without additional reagents *w.a.r.*

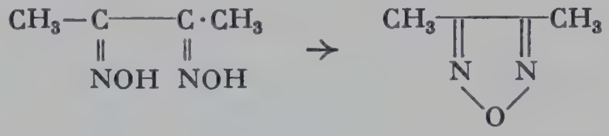
Benzisoxazoles from acyloximes ○
s. *7*, 161

Succinic anhydride



Furazans from glyoximes

115.



A mixture of dimethylglyoxime and succinic anhydride slowly heated, stirring commenced as soon as practicable, when the exothermic reaction starts at 150-170° the temp. kept in this range by removing the heater and cooling, then heating resumed and distilled at 160-200°, finally the residue steam-distilled → dimethylfurazan. Y: 60-64%.— The usual acid dehydrating agents fail. L. C. Behr and J. T. Brent, Org. Synth. *34*, 40 (1954).

Nitrogen ↑ ON⇑N

Without additional reagents *w.a.r.*

Isoxazole ring from o-azidoöxo compounds ○
s. *9*, 170

Benzofurazan oxides from o-nitroazides
s. *7*, 162

Formation of O—Hal Bond

Uptake

Addition to Halogen — OHal ⇓ Hal

Nitric acid — HNO_3

Iodoso compounds from iodides — $I \rightarrow IO$
s. *9*, 171

Hydrogen peroxide — H_2O_2

Iodosoacetates — $I(OAc)_2$
s. *9*, 172

Exchange

Hydrogen ↑ — OHal ⇅ H

Sodium hypochlorite — $NaOCl$

Alkyl hypochlorites from alcohols — $OH \rightarrow OCl$
s. 8, 139

Formation of O—S Bond

Uptake

Addition to Hydrogen and Oxygen — OS ⇓ HO

Triethylamine — $(C_2H_5)_3N$

Sulfuric acid esters from phenols — $OH \rightarrow OSO_3H$
s. 8, 140

Pyridine — C_5H_5N

Carbohydrate sulfuric acid esters
s. *6*, 146

Addition to Sulfur — OS ⇓ S

Peracetic acid — CH_3COO_2H

Sulfones from thioethers — $\rangle S \rightarrow \rangle SO_2$
s. 8, 141; s. a. H. Bohme and P. Heller, B. *86*, 785 (1953)

Perbenzoic acid — $C_6H_5COO_2H$
s. *9*, 173

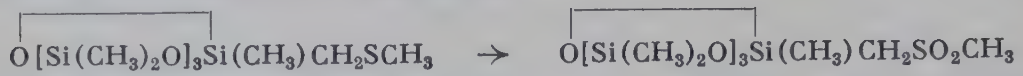
1,1-Disulfones from mercaptals — $C(SR)_2 \rightarrow C(SO_2R)_2$
s. *9*, 342

Disulfide monoxides — $\cdot SO \cdot S \cdot$
s. 7, 163

Perphthalic acid ←

Sulfones from thioethers $>S \rightarrow >SO_2$
Sulfonylmethylsilicon compounds

116.



$O[Si(CH_3)_2O]_3Si(CH_3)CH_2SCH_3 \rightarrow O[Si(CH_3)_2O]_3Si(CH_3)CH_2SO_2CH_3$

Heptamethyl(methanethiomethyl)cyclotetrasiloxane added dropwise to an ice-cooled soln. of monoperphthalic acid in ether, and allowed to stand 24 hrs. at room temp. after the initial vigorous reaction has subsided → heptamethyl(methanesulfonylmethyl)cyclotetrasiloxane. Y: 84%. F. e. s. G. D. Cooper, Am. Soc. *76*, 3713 (1954).

1,1-Disulfones from mercaptals $C(SR)_2 \rightarrow C(SO_2R)_2$
s. *7*, 324; also with perpropionic acid s. Am. Soc. *77*, 4348 (1955)

Iodosobenzene C_6H_5IO

Sulfoxides from thioethers $>S \rightarrow >SO$
s. *6*, 147

Nitric acid HNO_3

with simultaneous replacement of bromine by nitro groups
s. *8*, 500

Hydrogen peroxide H_2O_2

Sulfones from thioethers $>S \rightarrow >SO_2$
s. *6*, 148; s. a. J. L. Greene, Jr., and H. J. Hagemeyer, Jr., Am. Soc. *77*, 3016 (1955)

1,1-Disulfones from mercaptals $C(SR)_2 \rightarrow C(SO_2R)_2$
s. *10*, 480

Thiosulfonic acid esters from disulfides $RSSR \rightarrow RSO_2SR$

117. $CH_3SSCH_3 \rightarrow CH_3SO_2SCH_3$

2 moles 30%-H_2O_2 added slowly with stirring and cooling below 15° to a soln. of dimethyl disulfide in acetic acid, and stirring continued for 15 min. while the temp. is raised to 50° → methyl methanethiolsulfonate. Y: 70-80%. H. J. Backer, R. *67*, 902 (1948); Bl. Soc. chim. Belg. *62*, 3 (1953).

Hydrogen peroxide/acetic acid H_2O_2/CH_3COOH

2,3-Diazabuta-1,3-diene-1-sulfonic acids from thiosemicarbazones ←
s. *8*, 142

Chlorine Cl

Sulfonic acid chlorides from sulfenylchlorides, disulfides, mercaptans, or sulfinic acids ←
s. *8*, 143

Sodium permanganate *$NaMnO_4$*

Sulfonic from sulfinic acids $SO_2H \rightarrow SO_3H$
s. *7*, 164

Potassium permanganate *$KMnO_4$*

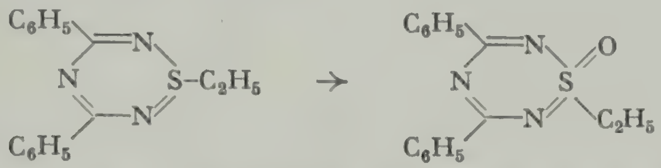
Sulfones from thioethers $\rangle S \rightarrow \rangle SO_2$

s. *6*, 148; s. a. Balasubramanian and V. Baliah, Soc. *1955*, 1251

Sulfoximides from sulfinimides ←
s. *7*, 165

1,2,4,6-Sulfinetriazine 1-oxides ←

8.



An aq. soln. of $KMnO_4$ containing some Na-carbonate added with ice-cooling to a soln. of 1-ethyl-3,5-diphenyl-1,2,4,6-sulfinetriazine in acetone, and the product isolated after several hrs. → 1-ethyl-3,5-diphenyl-1,2,4,6-sulfinetriazine 1-oxide. Y: 91%. F. e. s. J. Goerdeler and D. Loevenich, B. *87*, 1079 (1954).

Oxydations with
Ruthenium tetroxide *RuO_4*

Sulfones from thioethers $\rangle S \rightarrow \rangle SO_2$
s. *9*, 174

Exchange

Hydrogen ↑ OS⇅H

Without additional reagents *w.a.r.*

Sulfuric acid monoesters OSO_3H
s. *9*, 175; partial formation from diols s. G. Dupont, D. Dulou, and G. Lefèbvre, Bl. *1954*, 816

Resolution of racemates via salts
Optically active alcohols
via sulfuric acid ester salts
s. *9*, 176

Oxygen ↑ OS⇅O

Pyridine *C_5H_5N*

Sulfonic acid esters $OH \rightarrow OSO_2R$

$$C_6H_5OH \rightarrow C_6H_5OSO_2CH_3$$

A mixture of phenol and methane*sulfonic acid anhydride-pyridine complex* in dry benzene allowed to stand overnight, then refluxed 2 hrs.

→ phenyl methanesulfonate. Y: 85%.—A convenient and efficient means of removing sulfonic anhydrides from reaction mixtures is provided by treatment with pyridine to form the complex, and subsequent washing with dil. aq. $NaHCO_3$. L. Field and P. H. Settlage, Am. Soc. *76*, 1222 (1954).

Methoxyacetylene $HC:C{\cdot}OCH_3$

Sulfonic acid anhydrides from sulfonic acids $2\,RSO_3H \rightarrow (RSO_2)_2O$
s. *9*, 261

Reactions with
Carbodiimides $RN:C:NR$
s. *9*, 177

Phosphorus pentoxide P_2O_5
s. *9*, 178

Halogen ↑ OS ⇅ Hal

Potassium hydroxide KOH

Oxime sulfonates $C:NOSO_2R$
s. *9*, 179

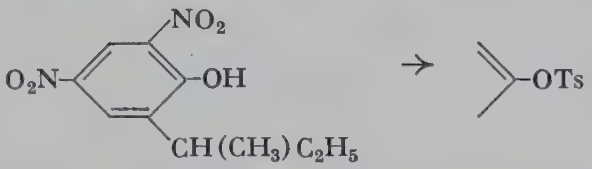
Sodium/alcohol $NaOR$

Sulfenic acid esters from sulfenylchlorides $SCl \rightarrow SOR$
s. *8*, 144

Potassium carbonate K_2CO_3

p-Toluenesulfonic acid esters from phenols $OH \rightarrow OSO_2C_7H_7$

120.

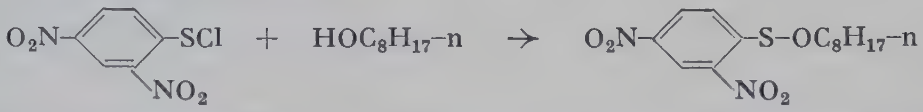


A mixture of DL-2-s-butyl-4,6-dinitrophenol, p-toluenesulfonyl chloride, and K-carbonate in dry acetone refluxed 14 hrs. with stirring → DL-2-s-butyl-4,6-dinitrophenyltosylate. Y: 94%. F. Hawthorne and D. J. Cram, Am. Soc. *74*, 5859 (1952); cf. Synth. Meth. *10*, 444.

Pyridine C_5H_5N

Sulfenic acid esters
from alcohols and sulfenylchlorides $OH \rightarrow OSR$
Characterization of alcohols

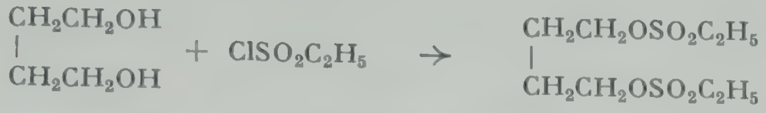
121.



2,4-Dinitrobenzenesulfenyl chloride and ethylene chloride swirled and gently heated until dissolved, n-octanol added, again swirled, pyridine added, swirled and allowed to stand 15-30 min. → n-octyl 2,4-dinitrobenzenesulfenate. Y: 90%. F. e. s. N. Kharasch, D. P. McQuarrie, and C. M. Buess, Am. Soc. *75*, 2658 (1953).

Mixed sulfurous acid esters

s. *10*, 643 SO(OR)(OR′)



$$\begin{matrix}CH_2CH_2OH\\ |\\ CH_2CH_2OH\end{matrix} + ClSO_2C_2H_5 \rightarrow \begin{matrix}CH_2CH_2OSO_2C_2H_5\\ |\\ CH_2CH_2OSO_2C_2H_5\end{matrix}$$

Diol bis(alkylsulfites). A soln. of ethyl chlorosulfite in chloroform added dropwise with stirring during 0.5 hr. to an ice-cooled soln. of tetramethylene glycol, pyridine, and chloroform, and left 1.5 hrs. in the bath → tetramethylene glycol bis(ethylsulfite). Y: 83.9%. F. e. s. D. C. Morrison, Am. Soc. *76*, 3224 (1954).

Sulfonic acid esters from alcohols

s. *7*, 589 OH → OSO_2R

Methanesulfonic acid esters from alcohols

s. *8*, 887 OH → OSO_2CH_3

Carbohydrate derivatives
Selective acylation s. *6*, 149

p-Toluenesulfonic acid esters

$OSO_2C_7H_7$

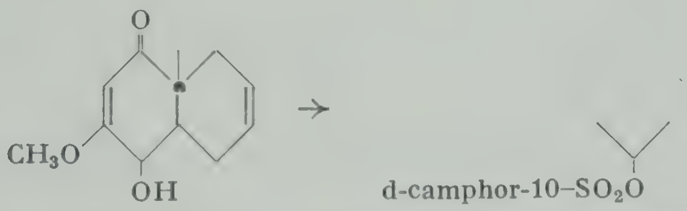
s. *10*, 17; at low temp. s. W. F. Edgell and L. Parts, Am. Soc. *77*, 4899 (1955)

as intermediates
s. *9*, 623

Partial O-tosylation
s. *9*, 825

Resolution of alcohols via d-camphor-10-sulfonic acid esters

OH → OSO_2R



Crude d,l-*trans*-1-hydroxy-4-keto-2-methoxy-10-methyl-$\Delta^{2,6}$-hexahydronaphthalene (prepn. s. 49) dissolved in anhydrous pyridine, treated portionwise with d-camphor-10-sulfonyl chloride during 15 min., the temp. allowed to rise to 60°, maintained 1 hr. at this temp., first by cooling and later by warming, and the crude sulfonate diastereoisomers (Y: 85-95%) separated by fractional crystallization from acetone → l-diastereoisomer (Y: ca. 90%) and d-diastereoisomer (Y: 80-85%) (startg. m. f. 81). A. J. Speziale, J. A. Stephens, and Q. E. Thompson, Am. Soc. *76*, 5011 (1954).

Sulfonylaminophenol sulfonic acid esters from aminophenols

s. *8*, 375

γ-Collidine ←

Sulfonic acid esters
from alcohols and sulfonic acid chlorides
s. *9*, 180

Mercuric oxide *HgO*

Sulfonic acid anhydrides $2\,RSO_2Cl \rightarrow (RSO_2)_2O$
from sulfonic acid chlorides
s. *9*, 181

Sulfur ↑ OS ⇅ S

Sodium hydroxide *NaOH*

Sulfinic acids from disulfides $RSSR \rightarrow 2\,RSO_2H$
s. *6*, 150

Elimination

Oxygen ↕ OS ⇑ O

Thionyl chloride $SOCl_2$

Carboxylic sulfonic acid anhydrides ←
s. *6*, 151

Formation of O—Rem Bond

Uptake

Addition to Hydrogen and Oxygen ORem ⇓ HO

Without additional reagents *w.a.r.*

Phosphorylation $OH \rightarrow OPO(OH)_2$
s. 7, 166; *8*, 250; s. a. R. H. Hall and H. G. Khorana, Am. Soc. *77*, 1871 (1955)

Aldehydes from hydrazones
s. *8*, 145

Pyridine C_5H_5N

of carbohydrates
s. *8*, 146

Addition to Hydrogen and Remaining Elements ORem ⇓ HRem

Via intermediates *v.i.*

Phosphinic acids from phosphine oxides $R_2P(O)H \rightarrow R_2P(O)OH$
s. *9*, 182

Addition to Oxygen and Carbon

ORem ⇓ OC

Without additional reagents

w.a.r.

Phosphoric acid esters from oxido compounds

C

s. *6*, 152

Addition to Remaining Elements

ORem ⇓ Rem

Nitric acid

HNO_3

Phosphorus(V) from phosphorus(III) compounds

←

Phosphinic acids
s. *8*, 702

Hydrogen peroxide

H_2O_2

s. *8*, 701

Phosphine oxides from phosphines
Phosphinic from phosphinous acids

P → P:O

s. *7*, 167

Arsine oxides from arsines

As → As:O

s. *6*, 153

Sulfuryl chloride

SO_2Cl_2

Phosphonic acid dichlorides
from dichlorophosphines

P → P:O

$$C_2H_5\overset{\times}{P}Cl_2 \rightarrow C_2H_5\overset{\times}{P}(O)Cl_2$$

P^{32}-Labeled compounds. Ethyldichlorophosphine-P^{32} allowed to react with SO_2Cl_2 in benzene in an enclosed system (s. original) → ethylphosphonic-P^{32} dichloride. Y: 80%. B. C. Saunders and T. S. Worthy, Soc. *1953*, 2115.

Exchange

Hydrogen ↑

ORem ⇵ H

Without additional reagents

w.a.r.

Sodio derivatives of carbohydrates

OH → ONa

Differential reactivity of hydroxyl groups
s. *9*, 183

Chlorophosphoric acid esters

$(RO)_2POCl$

s. *8*, 147

Dithiophosphoric acids

$(RO)_2PSSH$

s. *6*, 156

Lithium/alcohol

$LiOR$

Silicates from alcohols and silane

$Si(OR)_4$

s. *7*, 168

Pyridine

C_5H_5N

Dichlorophosphoric acid esters

$ROPOCl_2$

s. *7*, 174

Carbon tetrachloride/triethylamine *$CCl_4/(C_2H_5)_3N$*

Phosphoric acid esters from dialkylphosphites ←
Phosphorylation of phenols
s. *10*, 107

Oxygen ↑ ORem ⇅ O

Without additional reagents *w.a.r.*

Boric acid esters – Masking of hydroxyl groups $B(OR)_3$
s. *10*, 421; boric acid esters s. a. G. L. O'Connor and H. R. Nace, Am. Soc. *77*, 1578 (1955)

Germanium esters from germanium oxides ←
s. *8*, 148

Cyclic phosphoric acids ○
s. *8*, 149

Cyclic selenous acid esters
s. *7*, 338

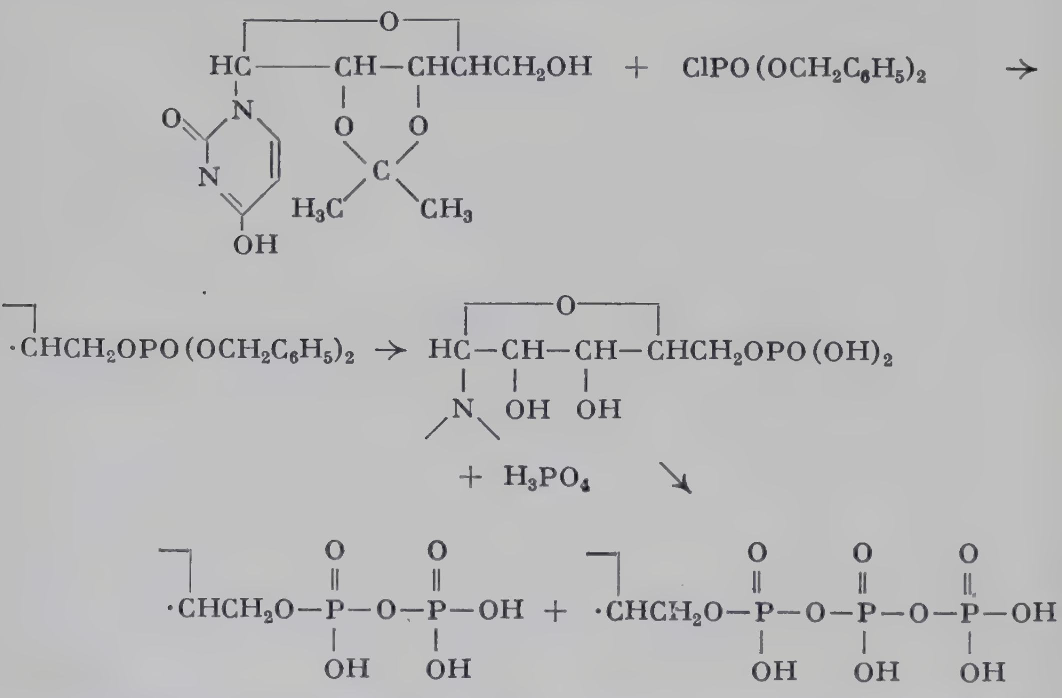
Carbodiimides *RN:C:NR*

Pyrophosphoric acid esters $(RO)_2PO·O·OP(OR)_2$
s. *9*, 184

Dicyclohexylcarbodiimide/pyridine *$RN:C:NR/C_5H_5N$*

Nucleotides ←
Di- and tri-phosphoric acids via phosphoric acids

125.



A concd. soln. of dibenzyl chlorophosphate in benzene added to a soln. of 2',3'-isopropylidene uridine in anhydrous pyridine prechilled in a

CO_2-acetone bath, kept partly immersed in the cold bath for 3 hrs., then 16 hrs. at room temp., the crude product hydrogenated 24-36 hrs. at ca. 12 p. s. i. with 10%-Pd-charcoal in ethanol-water-HCl, the catalyst removed by filtration, and the filtrate evaporated → uridine-5′-phosphate (Y: 81%) vigorously shaken for 2 hrs. with 85%-H_3PO_4 and dicyclohexylcarbodiimide in aq. pyridine, the aq. soln. of pyridine salts of the products passed through a Dowex-50 ion-exchange resin column, whereby the free acids are formed, the mixture of nucleotides separated on a Dowex-2 column, and the products isolated as the Ba-salts → uridine-5′-diphosphate (Y: 20-25%) and uridine-5′-triphosphate (Y: ca. 20%). R. H. Hall and H. G. Khorana, Am. Soc. *76*, 5056 (1954).

Nitrogen ↓

ORem ⇅ N

Without additional reagents

w.a.r.

Silicates from aminosilanes

←

s. *6*, 154

Halogen ↓

ORem ⇅ Hal

Without additional reagents

w.a.r.

Alkoxy- from halogeno-silanes and orthoformic acid esters

SiHal → SiOR

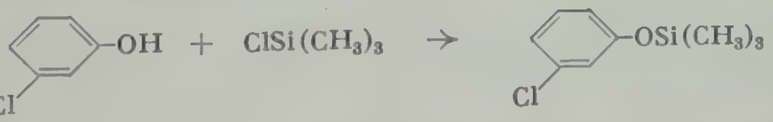
26.

$$\begin{gathered} CH_3SiHCl_2 \quad + \quad 2\ HC(OC_2H_5)_3 \\ \downarrow \\ CH_3SiH(OC_2H_5)_2 \quad + \quad 2\ C_2H_5Cl \quad + \quad 2\ HCOOC_2H_5 \end{gathered}$$

Methyldichlorosilane added to ethyl orthoformate, the temp. kept below 46° during the exothermic reaction, and the product isolated after 0.5 hr. → diethoxymethylsilane. Y: 82%.—The reaction is rapid and avoids the formation of hydrogen halide and its attendant by-products. F. e. s. L. M. Shorr, Am. Soc. *76*, 1390 (1954).

Aryloxy- from halogeno-silanes

7.



Excess trimethylchlorosilane added to m-chlorophenol, and refluxed 9 hrs. under anhydrous conditions → m-chlorophenoxytrimethylsilane. Y: 88%. R. A. Benkeser and H. R. Krysiak, Am. Soc. 75, 2421 (1953); method s. J. L. Speier, Am. Soc. 74, 1003 (1952).

$Si(OR)_4$

Orthosilicates

from alcohols s. *3*, 108; from phenols s. R. Schwarz and W. Kuchen, B. *86*, 1144 (1953)

Siloxanes from halogenosilanes $2\,{>}\mathrm{SiHal} \rightarrow {>}\mathrm{Si{\cdot}O{\cdot}Si}{<}$
s. *6*, 543

Phosphonous acid monoesters from dichlorophosphines $\mathrm{RPCl_2} \rightarrow \mathrm{RP}{<}^{\mathrm{OR'}}_{\mathrm{OH}}$
s. *7*, 659

Cyclic phosphites ○
s. *7*, 169

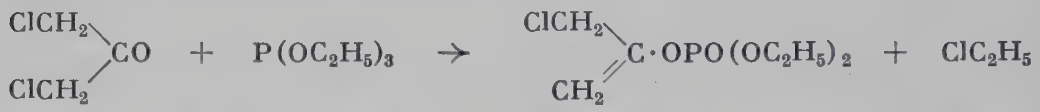
Dichlorophosphites $\mathrm{ROPCl_2}$
s. *7*, 170

Phosphonic acid esters from phosphinic acid esters via halogenophosphinic acid esters ←
s. *8*, 150

Phosphonic acid esters from phosphonyl dichlorides $\mathrm{RPOCl_2} \rightarrow \mathrm{RPO(OR')_2}$
s. *7*, 171

1-Ethylenephosphonic acid esters from α-halogenocarbonyl compounds ←

128.



$$\begin{matrix}\mathrm{ClCH_2}\\ \mathrm{ClCH_2}\end{matrix}{>}\mathrm{CO} + \mathrm{P(OC_2H_5)_3} \rightarrow \begin{matrix}\mathrm{ClCH_2}\\ \mathrm{CH_2}\end{matrix}{\gg}\mathrm{C{\cdot}OPO(OC_2H_5)_2} + \mathrm{ClC_2H_5}$$

Triethyl phosphite added gradually with cooling at 40-50° to sym. dichloroacetone, then the temp. raised to 100° → diethyl 1-(chloromethyl)-vinyl phosphate (Y: 82%) and ethyl chloride (Y: 85%). F. e. s. J. F. Allen and O. H. Johnson, Am. Soc. *77*, 2871 (1955).

Chloroseleninic acid esters $\mathrm{ClSeO(OR)}$
s. *7*, 172

Sodium hydride *NaH*

Alkoxy- from halogeno-silanes $\mathrm{SiHal} \rightarrow \mathrm{SiOR}$
s. *8*, 151

Sodium hydroxide *NaOH*

Siloxanes from fluorosilanes $2\,{>}\mathrm{SiF} \rightarrow {>}\mathrm{Si{\cdot}O{\cdot}Si}{<}$
s. *7*, 173

Germanium oxides from halogenogermanes $2\,{>}\mathrm{GeHal} \rightarrow {>}\mathrm{Ge{\cdot}O{\cdot}Ge}{<}$
s. *8*, 580

Germanecarboxylic acid germyl esters $\mathrm{R_3GeCOOGeR_3}$
s. *9*, 195

Potassium hydroxide *KOH*

Silanols from halogenosilanes $\mathrm{SiCl} \rightarrow \mathrm{SiOH}$
s. *6*, 155

Phosphoric acids
via dichlorophosphoric acid esters
s. 7, 174

$ROPOCl_2 \rightarrow ROPO(OH)_2$

Sodium/alcohol

$NaOR$

Phosphinic acid esters from phosphinic acid chlorides ←
s. 7, 175

Sodium carbonate

Na_2CO_3

Monothiophosphoric acid esters
via dithiophosphoric acids
and chlorothiophosphoric acid esters ←
s. 6, 156

Ammonia

NH_3

Titanic acid esters
s. 9, 185

$Ti(OR)_4$

Triethylamine

$(C_2H_5)_3N$

Peptide synthesis with chlorophosphites ←
s. 9, 475

Triethanolamine

$(HOCH_2CH_2)_3N$

Acoxy- from halogeno-silanes
s. 9, 186

$SiHal \rightarrow SiOAc$

Dialkylaniline

$C_6H_5NR_2$

Phosphites ←
s. 6, 157; s. a. J. F. Allen and O. H. Johnson, Am. Soc. 77, 2871 (1955)

Dimethylaniline

$C_6H_5N(CH_3)_2$

Alkoxy- from chloro-silanes

$SiCl \rightarrow SiOR$

$$(CH_3)_2SiCl_2 + 2\ CH_3OH \rightarrow (CH_3)_2Si(OCH_3)_2$$

A soln. of methanol and dimethylaniline added during 2 hrs. below the surface of a stirred soln. of dimethyldichlorosilane and dimethylaniline at a rate to maintain gentle refluxing → dimethyldimethoxysilane (startg. m. f. 4). Y: 60-70%. S. W. Kantor, Am. Soc. 75, 2713 (1953).

Pyridine

C_5H_5N

Reaction of boron trichloride with alcohols and ethers ←
Optically active compounds s. 8, 152

Siloxanols from halogenosilanes ←
s. 9, 187

Mixed phosphites
s. 9, 188

$(RO)_2P(OR')$

Phosphorylation of hydroxy compounds OH → OPO_3^{--}
s. *2*, 138; *7*, 174; cf. W. J. Gensler and A. P. Mahadevan, Am. Soc. *76*, 6192 (1954)

s. a. *9*, 189; *10*, 125; of carbohydrates s. J. L. Barclay, A. B. Foster. and W. G. Overend, Soc. *1955*, 2505

Hydrogenolysis of phosphoric acid esters
s. *6*, 158; s. a. P. A. J. Gorin, L. Hough, and J. K. N. Jones, Soc. *1955*, 582

Pyrophosphoric acid esters ←
s. *7*, 176

Dithionopyrophosphoric acid esters from halogenothionophosphoric acid esters ←
s. *8*, 153

Quinoline ←
Alkoxy- from chloro-silanes SiCl → SiOR
s. *10*, 446

Silver oxide Ag_2O
Selenenic acids from selenylbromides SeBr → SeOH
s. *9*, 190

Silver acetate CH_3COOAg
Selenenic acid esters from selenylbromides SeBr → SeOR
s. *8*, 154

Selenyl acetates from selenylhalides SeHal → SeOAc
s. *9*, 191

Methyl Cellosolve $HOCH_2CH_2OCH_3$
Silanols from halogenosilanes SiHal → SiOH
s. *9*, 192

Sulfur ↑ ORem ⇵ S

Without additional reagents *w.a.r.*
Thiophosphonic acids from dithiophosphonic acids $RPOS_2H_2 \rightarrow RPO_2SH_2$
s. *7*, 672

Dithiophosphoric acid esters from orthoformic acid esters ←
s. *9*, 193

Hydrogen peroxide H_2O_2
Seleninic acids and sulfonic acids from selenylsulfides ←
s. *6*, 159

Carbon ↑ ORem⇵C

Without additional reagents *w.a.r.*

Cleavage of mixed ethers – Dichloroboric acid esters ←
s. *9*, 194

Germanecarboxylic acid germyl esters $R_3GeCOOGeR_3$
s. *9*, 195

Organolead compounds ←
s. *7*, 177

Phosphinic acid anhydrides ←
s. *7*, 178

Potassium hydroxide *KOH*

Phosphine oxides from phosphonium salts ←
s. *9*, 196

Sulfuric acid H_2SO_4

Siloxanes from methylsilanes ←
s. *7*, 179

Hydrochloric acid *HCl*

Diboroxides $>B\cdot O\cdot B<$
s. *9*, 197

Formation of O—C Bond

Uptake

Addition to Hydrogen and Oxygen OC⇓HO

Hydrochloric acid *HCl*

Allophanates – Characterization of alcohols $OH \rightarrow OCONHCONH_2$
s. *8*, 155

Addition to Hydrogen and Carbon OC⇓HC

Irradiation ←

Hydroperoxides from hydrocarbons $H \rightarrow OOH$
s. *7*, 180

Electric discharge ←

Phenols from hydrocarbons $H \rightarrow OH$
s. *9*, 198

Sodium hydroxide *NaOH*

Cannizzaro reaction
Carboxylic acids and prim. alcohols from aldehydes $2\,CHO \rightarrow COOH+CH_2OH$
s. *7*, 67

Sodium hydroxide/potassium hydroxide *NaOH/KOH*

Carboxylic acids from aldehydes, also cleavage of ethers $CHO \rightarrow COOH$
s. *6*, 160

Sodium nitrite/nitric acid s. Nitric acid/sodium nitrite $NaNO_2/HNO_3$

Copper acetate/nickel acetate ←
s. Nickel acetate/copper acetate

Fungi ←

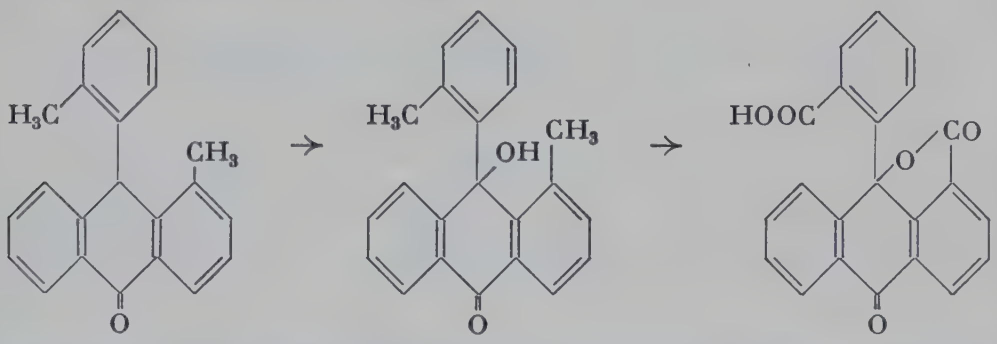
Alcohols from hydrocarbons – Bioöxygenation $H \rightarrow OH$

11α-Hydroxysteroids s. *7*, 181; 11β-hydroxysteroids s. G. M. Schull and D. A. Kita, Am. Soc. *77*, 763 (1955); 7α-, 15α-, or 15β-hydroxysteroids s. C. Meystre, E. Vischer, and A. Wettstein, Helv. *38*, 381 (1955)

Nitrobenzene/nitric acid $C_6H_5NO_2/HNO_3$

Oxanthranols from anthrones ←
Oxidation of methyl groups
Lactones from hydroxy compounds

130.



A mixture of 1-methyl-9-(o-tolyl)-10-anthrone (prepn. s. 652) and nitrobenzene refluxed 36 hrs. with HNO_3-soln. (d. 1.1) → 1-methyl-9-(o-tolyl)oxanthranol (Y: 95%), 3 g. heated under pressure with HNO_3-soln. (d. 1.12) at 200° for 10 hrs. → 2 g. 9-(o-carboxyphenyl)oxanthranol-1-carboxylic acid lactone (startg. m. f. 651). E. Clar and D. G. Stewart, Am. Soc. *75*, 2667 (1953).

Nitric acid HNO_3

2-Nitroalcohols from hydrocarbons $CHCH \rightarrow C(OH)C(NO_2)$
s. *10*, 289

Carboxylic acids from aldehydes $CHO \rightarrow COOH$
s. *8*, 156

Nitric acid/sodium nitrite *$HNO_3/NaNO_2$*
s. *6*, 170

Oxygen/manganese diacetate s. Manganese diacetate/oxygen *$O_2/(CH_3COO)_2Mn$*

Hydrogen peroxide *H_2O_2*

Replacement of hydrogen by hydroxyl H → OH
s. *7*, 182

Hydroperoxides/osmium tetroxide *$R{\cdot}OOH/OsO_4$*
s. Osmium tetroxide/hydroperoxides

Persulfate *$S_2O_8^{--}$*

Elbs reaction

with K-persulfate s. *9*, 199; aminosulfonic acids with NH_4-persulfate s. E. Bamann and K. Schriever, B. *86*, 996 (1953)

Selenium dioxide *SeO_2*

1,2,3-Hydroxydiketones from ketones ←
s. *9*, 230

Chromic acid *CrO_3*

Ketolactols from ketoöxido compounds ←
s. *9*, 200

Bromine *Br*

Aldonic acids from carbohydrates CHO → COOH
s. *6*, 161; in the presence of $CaCO_3$ s. a. R. Kuhn and H. H. Baer, B. *88*, 1537 (1955)

Iodine/potassium iodide *I/KI*

Carboxylic acids from aldehydes
s. *10*, 220

Manganese diacetate/oxygen *$(CH_3COO)_2Mn/O_2$*
s. *8*, 157

Potassium manganate and permanganate *K_2MnO_4 and $KMnO_4$*

Tert. hydroxycarboxylic acids from carboxylic acids H → OH
s. *9*, 201

Potassium permanganate *$KMnO_4$*

Ketocarboxylic acids from hydroxyaldehydes ←
s. *9*, 364

Nickel acetate/copper acetate ←

Carboxylic acids from aldehydes CHO → COOH
s. *6*, 292

Osmium tetroxide/hydroperoxides *$OsO_4/R{\cdot}OOH$*
s. *7*, 183

Via intermediates *v.i.*

Hydroxy compounds H → OH

via hydroperoxides
s. *8*, 158

via bromides and formoxy compounds
s. *8*, 159

α-Hydroxyketones from ketones
via enolesters and 1-acoxy-1,2-oxido compounds
17α-Hydroxy-20-ketosteroids s. *7*, 184; *9*, 202

o-Hydroxyethers from ethers
via xanthylium salts and xanthydrols
s. *6*, 162

o-Aminophenols from ar. amines
via o-aminosulfuric acid esters
s. *9*, 203

Addition to Oxygen OC ⇓ OO

Platinum, platinum oxide *Pt,* PtO_2

N-Heterocyclic hydroperoxides OOH
s. 8, 158; *9*, 204

Addition to Oxygen and Nitrogen OC ⇓ ON

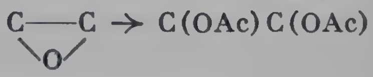
Sodium hydroxide *NaOH*

Isoxazole ring opening ↺
s. *9*, 205

Addition to Oxygen and Carbon OC ⇓ OC

Without additional reagents *w.a.r.*

Glycol esters from oxido compounds
s. *6*, 163



Ammonium hydroxycarboxylates from lactones
s. *10*, 260

Oxazolone ring opening
s. *6*, 164/5

Coumarin ring opening
s. *6*, 166

Epimerization of oxidosteroids ←
Double Walden inversion
Glycol monoesters from oxido compounds
s. *9*, 206

Irradiation ←

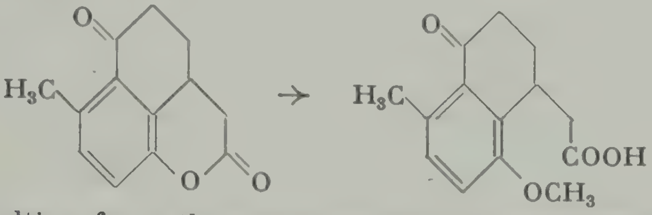
Quinol monoesters from quinones and aldehydes ←
s. *9*, 207

Sodium hydroxide *NaOH*

Ketocarboxylic acids from enollactones C
s. 7, 351

Oxazole ring opening
s. 6, 167

Coumarin ring opening

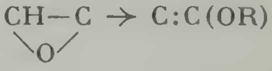
1.


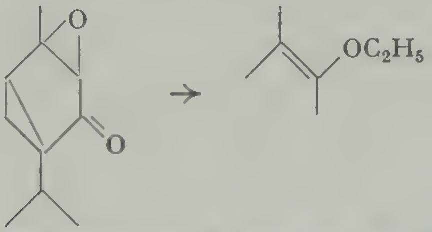
The soln. resulting from the gradual addition over a period of 1 hr., of dimethyl sulfate to a stirred soln. of 4-keto-5-methyl-8-hydroxy-1,2,3.4-tetrahydro-1-naphthylacetic acid lactone in aq.-methanolic NaOH refluxed 1 hr. → 4-keto-5-methyl-8-methoxy-1,2,3,4-tetrahydro-1-naphthylacetic acid (startg. m. f. 53). Y: 83%. A. S. Dreiding and A. J. Tomasewski, Am. Soc. *76*, 540 (1954).

Hydroxyacylamines from dihydrospiro-1,3-oxazines
s. 8, 413

Potassium hydroxide/alcohol *KOH*

Enolethers from oxido compounds

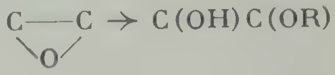

$\underset{\diagdown O \diagup}{CH{-}C} \rightarrow C{:}C(OR)$

2.


10 g. epoxyumbellulone refluxed 2 hrs. in alc. 5%-KOH → 7.6 g. α-ethoxyumbellulone. R. H. Eastman and J. C. Selover, Am. Soc. *76*, 4118 (1954).

Sodium/alcohol *NaOR*

Hydroxyethers from oxido compounds
s. 8, 263


$\underset{\diagdown O \diagup}{C{-}{-}C} \rightarrow C(OH)C(OR)$

Alkoxycarboxylic acids from lactones with subsequent hydrolysis of carboxylic acid esters C

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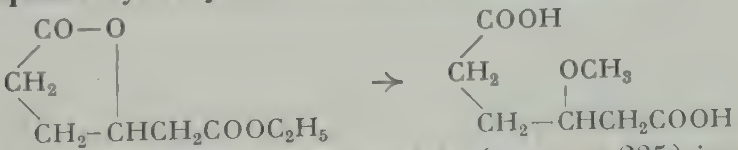


A soln. of d,l-5-carbethoxy-4,1-pentanolide (prepn. s. 235) in methanolic Na-methoxide allowed to stand 24 hrs. at room temp., water added, and allowed to stand 24 hrs. longer → d,l-3-methoxyadipic acid. Y: 79%. M. Viscontini and H. Köhler, Helv. *37*, 41 (1954).

Hydroxycarboxylic acid esters and alkoxycarboxylic acids from lactones
s. *8*, 160

Dicarboxylic acid monoesters from dicarboxylic acid anhydrides
s. *9*, 368

Coumarin ring opening
s. *8*, 75

Oxazolone ring opening
s. *6*, 757

β,β-Dialkoxy-α-acylaminocarboxylic acids from 4-alkoxymethyleneoxazolones
s. *8*, 161

Sodium acetate CH_3COONa

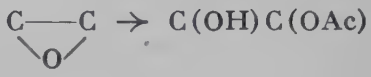
Oxazolone ring opening ↺
s. *4*, 152; s. a. X. A. Dominguez et al., Am. Soc. *77*, 1288 (1955)

Dimethylaniline $C_6H_5N(CH_3)_2$

Alkoxyhalogenhydrins ←
s. *8*, 162

Pyridine C_5H_5N

Glycol monoesters from oxido compounds
s. *9*, 208



$$\underset{\diagdown O \diagup}{C\!-\!C} \rightarrow C(OH)C(OAc)$$

Carboxyperoxycarboxylic acid esters from dicarboxylic acid anhydrides and hydroperoxides ↺
s. *9*, 209

Silver oxide Ag_2O

Hydroxybetaines from quaternary lactoneammonium salts
s. *9*, 210

Zinc Zn

Reductive acylation ←

Diacylquinols from quinones
s. *7*, 185/6

N-Heterocyclics
s. *8*, 556

Alumina Al_2O_3

Ethylenediols from ethyleneoxido compounds ←
11α-Hydroxysteroids s. *8*, 166

Aluminum alkoxide $Al(OR)_3$

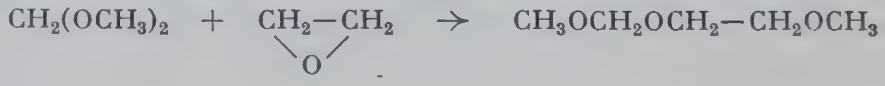
Carboxylic acid esters from 2 aldehyde molecules
Mixed Tishchenko reaction ←
s. *9*, 211

Boron fluoride BF_3

1,1-Di(acoxy) compounds from oxo compounds $CO \rightarrow C(OAc)_2$
s. *7*, 187

Alkoxyacetals from oxido compounds ←

134.



$$CH_2(OCH_3)_2 + \underset{\diagdown O \diagup}{CH_2\!-\!CH_2} \rightarrow CH_3OCH_2OCH_2\!-\!CH_2OCH_3$$

Liq. ethylene oxide gradually added with stirring at 0° to a soln. of BF_3 in 3 molar equivalents of methylal → 1-methoxymethoxy-2-methoxyethane. Y: 53%.—1:1 addition is favored by maintaining a considerable excess of the acetal. F. e. and higher addition products s. O. C. Dermer and A. M. Durr, Jr., Am. Soc. *76*, 912 (1954).

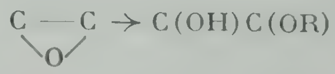
Peracetic acid/cobalt(II) acetate $CH_3COO_2H/(CH_3COO)_2Co$
s. Cobalt(II) acetate/peracetic acid

Acetyl chloride CH_3COCl

Dicarboxylic acid esters from dicarboxylic acid anhydrides C
s. *8*, 163

Stannic chloride $SnCl_4$

Halogenohydroxyethers from oxidohalides
s. *7*, 188



$\underset{O}{C - C} \rightarrow C(OH)C(OR)$

Nitrous acid/nitric acid HNO_2/HNO_3

Oxidative furan ring opening C
s. *6*, 168

Nitric acid HNO_3
s. *6*, 169

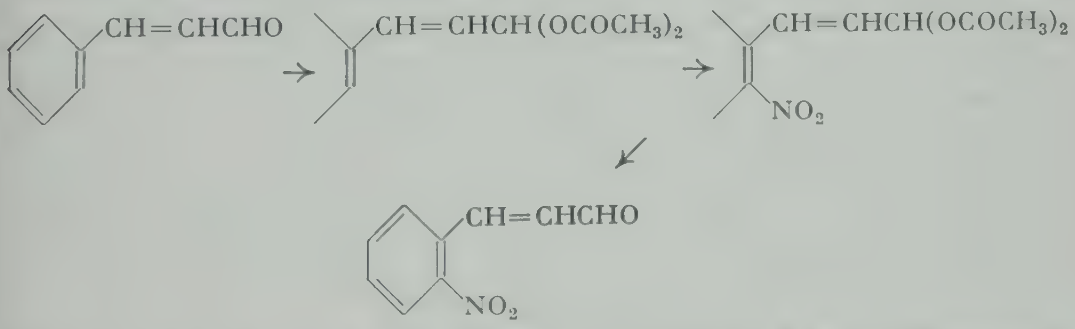
Glutaric acids – Pyran ring opening
s. *6*, 170

Phosphorus/hydriodic acid s. Hydriodic acid/phosphorus P/HI

Phosphoric acid H_3PO_4

Nitration of aldehydes $CHO \rightarrow CH(OAc)_2$
Protection of aldehyde groups
by formation of 1,1-diacetates

5.



H_3PO_4 (d. 1.75) added with stirring and cooling to a soln. of cinnamaldehyde in acetic anhydride, after 1 hr. HNO_3 (d. 1.52) added during 30 min. to the resulting diacetate (Y: 95-97% when isolated) soln. which is kept at −5 to 0° by addition of Dry Ice, then allowed to reach room temp. during 2 hrs. with stirring, poured into ice-water, HCl (d. 1.16) added during 15 min., allowed to stand overnight, the product dissolved in ethanol, aq. H_2SO_4 added, and refluxed 2 hrs. → o-nitrocinnamaldehyde (startg. m. f. 394). Y: 84%. F. 1,1-diacetates s. W. Davey and J. R. Gwilt, Soc. *1955*, 1384.

Thionyl chloride *$SOCl_2$*

Dicarboxylic acid monoesters
from dicarboxylic acid anhydrides
with cis-trans-rearrangement
s. *8*, 164

p-Toluenesulfonic acid *TsOH*

Dicarboxylic acid esters from dicarboxylic acid anhydrides
s. *6*, 171

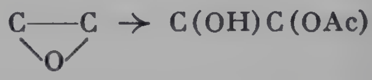
β-Ketocarboxylic acid esters from ketenedimers ←
via 6-keto-1,3-diox-4-enes
s. *9*, 212

Sulfuric acid *H_2SO_4*

Hydroxyquinols from quinones via triacoxyisocyclics ←
Thiele reaction
s. *8*, 165

Ethylenediols from ethyleneoxido compounds ←
11α-Hydroxysteroids s. *8*, 166

Glycol monoesters from oxido compounds
s. *10*, 528



$\mathrm{C{-}C(-O-)} \rightarrow \mathrm{C(OH)C(OAc)}$

Acidolysis of acetals ↺
s. *7*, 189

Acoxycarboxylic acids and derivatives from lactones
s. *7*, 190

Chlorosulfonic acid *$ClSO_3H$*

Dicarboxylic acid esters from dicarboxylic acid anhydrides
s. *8*, 227

Chromic acid *CrO_3*

Oxidative furan ring opening
s. *8*, 167

Potassium hypobromite *KOBr*

Ketocarboxylic acids from lactones
s. *9*, 213

Perchloric acid *$HClO_4$*

Thiele reaction ←
s. *8*, 165

Hydrochloric acid *HCl*

γ-Ketocarboxylic acid esters from furylcarbinols ↺
Allyl rearrangement – Ethers from alcohols
s. *7*, 191

136. **Synthesis with addition of 5 C-atoms.** A 5 C-atom chain lengthening can be achieved by a Grignard synthesis with halides and furfural and subsequent ring opening of the resulting furylcarbinols (cf. Synth. Meth. *7*, 191). E. s. G. Weitzel and J. Wojahn, H. *287*, 65 (1951).

Pyran ring opening
s. *6*, 172

Tetrahydropyran ring opening
s. *8*, 168

Hydriodic acid/phosphorus *HI/P*

Reductive coumarin ring opening
α-Aminocarboxylic acids from coumarins
s. *9*, 214

Potassium permanganate $KMnO_4$

Ketocarboxylic acids from lactones
s. *9*, 213

Cobalt(II) acetate/peracetic acid $(CH_3COO)_2Co/CH_3COO_2H$

Oxidative ring opening
s. *6*, 173

Platinum oxide/hydrobromic acid PtO_2/HBr

Reductive methylation of steroid ketones CO → CH(OR)
s. *9*, 215

Via intermediates *v.i.*

Quinolethers from quinones via quinols ←
s. *7*, 192

Addition to Nitrogen and Carbon OC⇓NC

Without additional reagents *w.a.r.*

Carboxylic acid amides from nitriles CN → $CONH_2$
s. *9*, 216

Urethans from alcohols OH → OCONHR
s. *7*, 517

Hydroxylactone derivatives
s. *7*, 193

Acylcarbamates from isocyanates NCO → NHCOOAc
s. *6*, 174

Pyrido[1,2-a]pyrimid-2-one ring opening ⊂
Tert. amines from betaines
s. *9*, 217

Sodium hydroxide *NaOH*

Pseudobases from cyclic quaternary ammonium salts ←
s. *6*, 820; *10*, 187

Lactam ring opening ⊂
s. *8*, 450

Azetidinone ring opening
s. *7*, 194

Pyridone ring opening
s. *6*, 175

Selective hydrolysis with preservation of the penicillin ring system
s. *9*, 218

Imidazolidine ring opening
s. *8*, 169

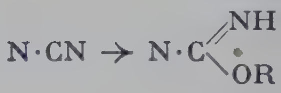
Potassium hydroxide KOH

Carboxylic acid amides from nitriles $CN \rightarrow CONH_2$
s. *7*, 195

Ureas from cyanamides $NHCN \rightarrow NHCONH_2$
s. *10*, 351

Sodium/alcohol $NaOR$

Isoureas from cyanamides
s. *6*, 176


$N{\cdot}CN \rightarrow N{\cdot}C\begin{smallmatrix}\nearrow NH \\ \searrow OR\end{smallmatrix}$

Nitric acid HNO_3

Acylguanylureas and acylbiurets from acyldicyanodiamides ←
s. *9*, 219

Polyphosphoric acid $H(PO_3H)_xOH$

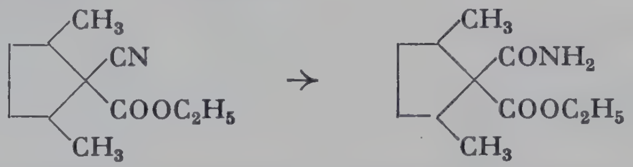
Carboxylic acid amides from nitriles $CN \rightarrow CONH_2$
s. *9*, 220

Sulfuric acid H_2SO_4

s. *6*, 177; *9*, 221, 583; α-aminocarboxylic acid amides s. C. B. Pollard and L. J. Hughes, Am. Soc. *77*, 40 (1955)

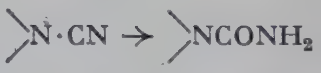
Dicarboxylic acid amide esters from cyanocarboxylic acid esters

137.



85%-H_2SO_4 added dropwise during 15 min. to ethyl d,l-1-cyano-2,5-dimethylcyclopentanecarboxylate heated in a boiling water bath, and heating continued for another 15 min. → ethyl d,l-1-carbamyl-2,5-dimethylcyclopentanecarboxylate. Y: 74%. F. e. s. C. J. Morel and W. G. Stoll, Helv. *35*, 2561, 2556 (1952).
s. a. *9*, 559

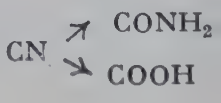
Ureas from cyanamides
s. *9*, 222


$>N{\cdot}CN \rightarrow >NCONH_2$

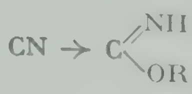
S-Thiocarbamic acid esters from thiocyanates $SCN \rightarrow SCONH_2$
s. *7*, 196

Hydrochloric acid HCl

Carboxylic acid amides and carboxylic acids from nitriles
s. *8*, 170

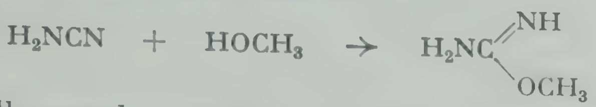

$CN\begin{smallmatrix}\nearrow CONH_2 \\ \searrow COOH\end{smallmatrix}$

Iminoesters from nitriles
s. *8*, 251



$CN \rightarrow C\begin{smallmatrix}=NH\\ -OR\end{smallmatrix}$

Isoureas from alcohols and cyanamide



$H_2NCN + HOCH_3 \rightarrow H_2NC\begin{smallmatrix}=NH\\ -OCH_3\end{smallmatrix}$

Anhydrous HCl passed at room temp. with ice-cooling into a soln. of cyanamide (prepn. s. original) in methanol, allowed to stand 3-4 days, then excess methanol removed by distillation under reduced pressure → methylisourea hydrochloride. Y: 69-80%. F. Kurzer and A. Lawson, Org. Synth. *34*, 67 (1954).

Acylguanylureas from acyldicyanodiamides
$CN \rightarrow CONH_2$
s. *9*, 219

Carbalkoxyguanylureas from carbalkoxydicyanodiamides
s. *9*, 562

Aminocarboxylic acids from lactams
C
s. *8*, 171; *9*, 555

Indolizine ring opening
s. *8*, 872

Imidazolidine ring opening
s. *8*, 169

Aminodithiolcarbonic acid esters from thiazolines
s. *9*, 705

Hydrobromic acid *HBr*

α-Hydroxycarboxylic acid amides from cyanohydrins
$CN \rightarrow CONH_2$
s. *10*, 333

Addition to Sulfur and Carbon OC ⇓ SC

Without additional reagents *w.a.r.*

Thiazoline ring opening
C
s. *9*, 223

Potassium hydroxide *KOH*

o-Mercaptophenylacetic acids from thianaphthenequinone 3-hydrazones
s. *9*, 121

Pyridine C_5H_5N

Acoxythiolic acid esters from ethylene sulfides
Direction of ring opening
s. *7*, 197

Hydrogen peroxide/acetic acid H_2O_2/CH_3COOH

Sulfonic acid esters from thioethers
$SR \rightarrow OSO_2R$
s. *9*, 224

Hydrochloric acid *HC*

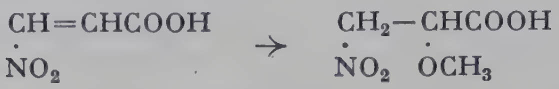
Thiazole ring opening C
s. *6*, 178

Addition to Carbon OC ⇓ C

Without additional reagents *w.a.r*

Ethers from ethylene derivatives C:C → CHC(OR

139.



$$\underset{NO_2}{CH}{=}CHCOOH \rightarrow \underset{NO_2}{CH_2}{-}\underset{OCH_3}{CH}COOH$$

A mixture of 3-nitroacrylic acid and anhydrous methanol refluxed hrs. → 2-methoxy-3-nitropropionic acid. Y: ca. 100%. H. Shechter e al., Am. Soc. *74*, 3052 (1952).

Reactions with carbon suboxide ←
Malonic acid esters
s. *7*, 198

Benzo-1,4-dioxane ring from ketenes and o-quinones C
s. *8*, 172

Sodium *N*

Ethers from ethylene derivatives C:C → CHC(OR
s. *6*, 179

Potassium

Vinylation H → CH:CH

140. $H_2NCH_2CH_2OH + HC{\equiv}CH \quad H_2NCH_2CH_2OCH{=}CH_2$

K added slowly to 2-aminoethanol, placed in an autoclave with benzene, acetylene admitted to 14-16 atm., heated 4-6 hrs. at 120-140°, cooled to 20-30°, the acetylene pressure restored, and heating repeate until the theoretical amount is consumed → crude 2-aminoethyl viny ether. Y: 85%. M. F. Shostakovskiĭ et al., Sint. Org. *2*, 33 (1952); C. A *48*, 563a; N-vinylation s. Sint. Org. *2*, 44; C. A. *48*, 584e; S-vinylatio s. Sint. Org. *2*, 54; C. A. *48*, 552f; f. e. s. in the same volume.

Sodium hydroxide *NaOH*

Alkoxyaldehydes from ethylenealdehydes C:C → CHC(OR
s. *9*, 225

Ketocarboxylic acids from cyclic acylketones C
s. *9*, 226

Sodium hydroxide/alcohol

γ,δ-Ethylene-β-ketocarboxylic acids ←
from α,β-acetylene-δ-hydroxycarboxylic acids
s. *7*, 199

Sodium hydroxide/hydrazine s. Hydrazine/sodium hydroxide *NaOH/H₂N·NH*

Potassium hydroxide *KOH*

Vinyl ethers OH → OCH:CH$_2$
s. *6*, 180

Hydrolytic ring opening of isocyclics C
s. *9*, 772

Hydrazones from azo compounds
s. *7*, 406

Potassium hydroxide/alcohol

3-Alkoxy-2,3-dihydrothianaphthene 1,1-dioxides from thianaphthene 1,1-dioxides C:C → CHC(OR)
s. *6*, 181

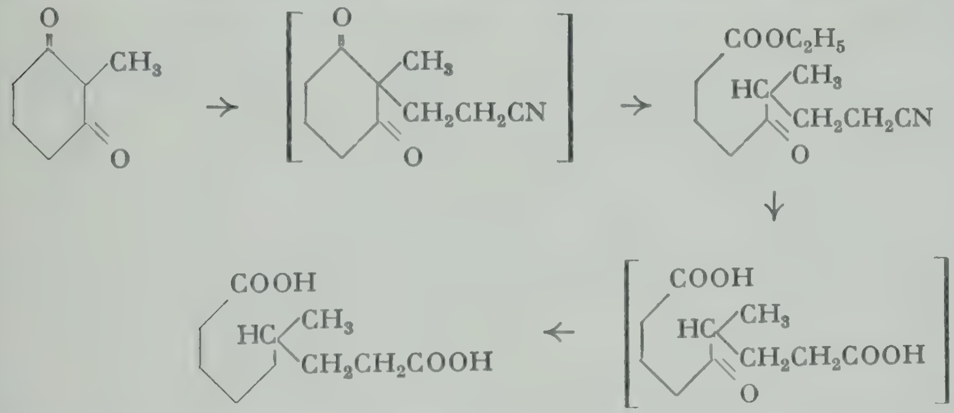
Sodium/alcohol *NaOR*

Ethers from ethylene derivatives
s. *7*, 200

Acetals from enolethers ←
α-Halogenacetals s. *6*, 182

Synthesis of long-chain α,ω-dicarboxylic acids from cyclic β-diketones via cyanoketocarboxylic acid esters C

1.



1-Methyl-2,6-cyclohexanedione and acrylonitrile added to a soln. of Na in abs. alcohol, and refluxed 10 hrs. → ethyl 7-cyano-4-oxo-5-methylheptane-1-carboxylate (Y: 63%) added with 85%-hydrazine to a soln. of NaOH in diethylene glycol, refluxed 4 hrs. whereby the temp. is kept at 115° by addition of small amounts of methanol, the resulting water, methanol, and excess hydrazine hydrate distilled off until the temp. reaches 195°, and refluxed 15 hrs. at this temp. → crude γ-methylazelaic acid (Y: 95%). F. e. s. H. Stetter and M. Coenen, B. 87, 990 (1954).

Sodium acetate *CH$_3$COONa*

Acetylation with ketene OH → OCOCH$_3$
s. *6*, 366

Enolesters from acetylene derivatives C⋮C → CH:C(OAc
s. *7*, 201

Sodium salt *Na+*

Vinyl esters COOH → COOCH:CH
from carboxylic acids and acetylene

142. $CF_3CF_2COOH + HC{\equiv}CH \rightarrow CF_3CF_2COOCH{=}CH_2$

Pentafluoropropionic acid sealed with a small amount of its Na-salt and an excess of acetylene in a Pyrex tube, then heated 12 hrs. at 220-240° → vinyl pentafluoropropionate. Y: 75%. R. N. Haszeldine and K. Leedham, Soc. *1953*, 1548.

Triton B ←

O-Cyanoethylation OH → OCH_2CH_2C

143. $BrCH_2[CH_2]_9CH_2OH + CH_2{=}CHCN \rightarrow BrCH_2[CH_2]_9CH_2OCH_2CH_2CN$

Acrylonitrile added at 32-36° during 10 min. to a soln. of 11-bromo-1-undecanol (prepn. s. 421) in *tert*-butanol containing Triton B, stirring continued for 20 min., the temp. raised to 50° during 0.5 hr., and stirred an additional hr. at this temp. → 15-bromo-4-oxapentadecanonitrile Y: 89%. F. e. s. M. G. J. Beets and W. Meerburg, R. *72*, 411 (1953).

Triethylamine $(C_2H_5)_3N$

O-Acetoacetylation OH → $OCOCH_2COCH$
s. *9*, 954

Silver oxide/ozone s. Ozone/silver oxide Ag_2O/O

Silver arylcarboxylate/iodine *ArCOOAg/I*

trans-Glycols from ethylene derivatives C:C → C(OH)C(OH
s. *6*, 183

Barium hydroxide $Ba(OH)$

Ketocarboxylic acids from cyclic β-diketones
Synthesis with addition of 6 C-atoms
s. *7*, 202

Mercuric oxide/boron fluoride HgO/BF

Ketones from acetylene derivatives C⋮C → COCH
s. *9*, 933; s. a. N. A. Dobson and R. A. Raphael, Soc. *1955*, 3558

Mercuric oxide/sulfuric acid HgO/H_2SO

s. *2*, 161; s. a. G. W. Stacy and R. A. Mikulec, Org. Synth. *35*, 1 (1955)

Mercury-resin ←

α-Hydroxyketones from α,β-acetylenealcohols
s. *9*, 102

Mercuric salt Hg^{++}

s. *8*, 173; β-ketoamines s. M. Koulkes, Bl. *1954*, 39

Boron fluoride/hydrogen fluoride BF_3/HF

Carboxylic acid esters and ethers ←
from ethylene derivatives
s. *8*, 174

Lithium aluminum hydride/ozone *$LiAlH_4/O_3$*
s. Ozone/lithium aluminum hydride

Benzaldehyde/oxygen s. Oxygen/benzaldehyde *C_6H_5CHO/O_2*

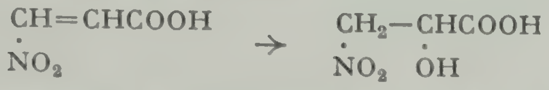
Amberlite ←

Cyanoethylation H → CH_2CH_2CN
s. *9*, 749

Formic acid *HCOOH*

Alcohols from ethylene derivatives C:C → CHC(OH)

14.



$$\underset{NO_2}{CH}{=}CHCOOH \rightarrow \underset{NO_2}{CH_2}{-}\underset{OH}{CH}COOH$$

A soln. of 3-nitroacrylic acid in 70%-formic acid heated 3 hrs. at 85-100° → 2-hydroxy-3-nitropropionic acid. Y: 83%. H. Shechter et al., Am. Soc. *74*, 3052 (1952).

Performic acid *$HCOO_2H$*

Glycols from ethylene derivatives C:C → C(OH)C(OH)
s. *7*, 239

Peracetic acid *CH_3COO_2H*

α-Branched carboxylic acids from acetylene derivatives with rearrangement ←

5. $n{-}C_4H_9{\cdot}C{\equiv}C{\cdot}C_4H_9{-}n \rightarrow (n{-}C_4H_9)_2CHCOOH$

12%-Peracetic acid added to 20 g. dibutylacetylene, kept at 25° with initial cooling until titration indicates completion of the reaction, and the resulting acid purified via its ester → 12 g. di-n-butylacetic acid. F. e. s. V. Franzen, B. *87*, 1219 (1954).

Peracetic acid/ozone s. Ozone/peracetic acid *CH_3COO_2H/O_3*

Trifluoroperacetic acid *CF_3COO_2H*

Glycols from ethylene derivatives C:C → C(OH)C(OH)

$CH_3[CH_2]_9CH{=}CH_2 \rightarrow CH_3[CH_2]_9CH(OH)CH_2OH$

Peroxytrifluoroacetic acid has been found to be a superior reagent for olefin hydroxylation. The reagent is particularly useful for prepn. of water soluble α-glycols and for hydroxylation of negatively subst. olefins.—E: 90%-H_2O_2, then trifluoroacetic anhydride in one portion added to ice-cooled methylene chloride, stirred 5 min. in the ice bath, added dropwise during 20 min. to a stirred soln. of 1-dodecene and *triethylammonium trifluoroacetate* in methylene chloride, and allowed to stand 15 min. at room temp. → 1,2-dodecanediol. Y: 95%.—Similarly: Oleic acid → 9,10-dihydroxystearic acid. Y: 92%. F. e. s. W. D. Emmons, A. S. Pagano, and J. P. Freeman, Am. Soc. *76*, 3472 (1954).

Trifluoroperacetic acid/disodium hydrogen phosphate *CF_3COO_2H/Na_2HPO_4*

Carboxylic acid esters from ketones RCOR′ → RCOOR′

147. $CH_3COCH(CH_3)C_2H_5 \rightarrow CH_3COOCH(CH_3)C_2H_5$

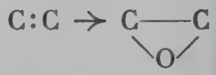
Trifluoroacetic anhydride added dropwise to a suspension of 90%-H_2O_2 in cold methylene chloride, the resulting soln. of peroxytrifluoroacetic acid added during 20 min. to a stirred suspension of dry Na_2HPO_4 in a mixture of methyl isobutyl ketone and methylene chloride with vigorous boiling caused by the exothermic reaction, finally refluxed 30 min. → isobutyl acetate. Y: 84%. F. e. s. W. D. Emmons and G. B. Lucas, Am. Soc. *77*, 2287 (1955).

Perbenzoic acid *$C_6H_5COO_2H$*

Stereoisomeric glycols from enolesters ←
via 1-acoxy-1,2-oxido compounds and α-acoxyketones
s. *9*, 227

Ketones from ethylene derivatives C:CH → CHCO
s. *6*, 184

Oxido compounds from ethylene derivatives



$C{:}C \rightarrow \underset{O}{C—C}$

Partial formation of oxido compounds s. *7*, 205; stereoisomeric α,β-oxidoketones s. H. H. Wasserman and N. E. Aubrey, Am. Soc. *77*, 590 (1955)

1,2-Oxidoacylamines from enacylamines
s. *10*, 175

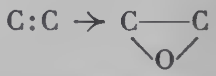
Ketolactams by oxidative ring opening C
s. *8*, 175

Perphthalic acid ←

α-Hydroxyketones from enolesters C:C(OAc) → C(OH)CO
s. *7*, 184; *9*, 202

γ-Hydroxy-α,β-ethyleneketones from (dien)olesters ←
s. *8*, 305

Oxido compounds from ethylene derivatives



$C{:}C \rightarrow \underset{O}{C—C}$

s. *2*, 165; simplified prepn. of perphthalic acid soln. s. E. E. Royals and L. L. Harrell, Jr., Am. Soc. *77*, 3405 (1955)

Red lead oxide *Pb_3O_4*

Ketones from ethylene derivatives C:CH → CHCO
via glycol diacetates
s. *6*, 185

Hemiquinolesters from phenols and reverse reaction ←
s. *7*, 206

Lead acetate/oxygen $(CH_3COO)_2Pb/O_2$

Oxidation of phloroglucinols ←

s. *8*, 176

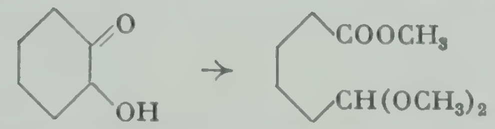
Lead tetraacetate $(CH_3COO)_4Pb$

Oxidative ring opening – Criegee cleavage ⊂

s. *7*, 207; *8*, 177; dialdehydes s. K. Alder and H. A. Dortmann, B. *87*, 1905 (1954)

gem-Dialkoxycarboxylic acid esters from cyclic acyloins

48.



Small portions of Pb-tetraacetate added with shaking and cooling to a soln. of 2-hydroxycyclohexanone in methanol until a slight excess persists for 10 min., as shown by starch-iodide paper, this excess destroyed by addition of a few drops of glycerol, a soln. of concd. H_2SO_4 in methanol added to catalyze the reaction of the aldehydoacid with methanol, allowed to stand 2 days in a stoppered flask → methyl 6,6-dimethoxyhexanoate. Y: 65%. F. e. s. C. D. Hurd and W. H. Saunders, Jr., Am. Soc. *74*, 5324 (1952).

Lead tetraacetate/potassium carbonate $(CH_3COO)_4Pb/K_2CO_3$

Oxidative ring opening

s. *6*, 842

Hydrazine/sodium hydroxide $H_2N{\cdot}NH_2/NaOH$

Carboxylic acids from cyclic β-diketones

Acid cleavage with subsequent Huang-Minlon reduction

Synthesis of long chain carboxylic and α,ω-dicarboxylic acids

s. *9*, 228; s. a. B. *87*, 1617 (1954)

Oxidations with

Nitrous oxide N_2O

Carboxylic acid amides from acetylene derivatives ←

s. *8*, 178

Nitric acid HNO_3

Quinones ←

s. *7*, 208

Phosphoric acid H_3PO_4

Bis-(2-furyl) oxides ←

s. *8*, 179

Phosphorus oxychloride $POCl_3$

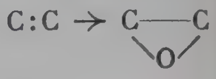
Acetals from enolethers ←

Protection of hydroxyl groups

s. *7*, 209

Oxygen/benzaldehyde *O_2/C_6H_5CHO*

Oxido compounds from ethylene derivatives

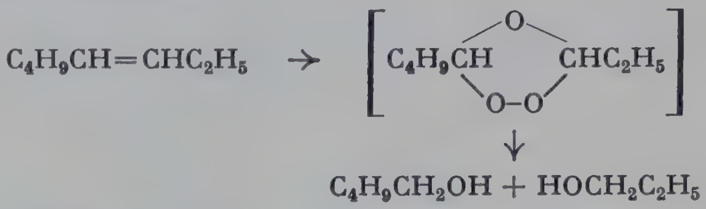


Coöxidation
s. *7*, 210

Ozone *O_3*

Alcohols from ethylene derivatives by cleavage via ozonides ←

149.



$C_4H_9CH{=}CHC_2H_5 \rightarrow [\text{ozonide}] \rightarrow C_4H_9CH_2OH + HOCH_2C_2H_5$

Ozonized O_2 passed at –42 to –38° through a solution of 3-octene in n-pentane for ca. 10 hrs., at the conclusion of the ozonization dry N_2 passed through at the same temp. to remove dissolved O_2, treated cautiously below –10° during 2 hrs. with an ethereal soln. of $LiAlH_4$, allowed to warm slowly, refluxed 15 min., kept overnight at room temp., and decomposed below –7° with aq. H_2SO_4 → n-propyl alcohol (Y: 87.4%) and n-amyl alcohol (Y: 87.0%). F. e. s. F. L. Greenwood, J. Org. Chem. *20*, 803 (1955).

Oxidative ring opening C

Removal of a protective group from the hydroxyl groups at C-atoms 1 and 2 of aldopyranoses

Deacetylation
s. *9*, 229

of indoles
s. *2*, 168; s. a. R. R. Brown and J. M. Price, Am. Soc. *77*, 4158 (1955)

Ozone/silver oxide *O_3/Ag_2O*
s. *7*, 211

Ozone/lithium aluminum hydride *$O_3/LiAlH_4$*

Diols
s. *7*, 204

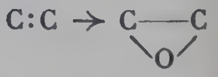
Ozone/peracetic acid *O_3/CH_3COO_2H*

Cleavage of ozonides
s. *6*, 186

Hydrogen peroxide *H_2O_2*

Ketones from ethylene derivatives C:CH → CHCO
s. *8*, 180

α,β-Oxidoketones from α,β-ethyleneketones



s. *6*, 192, 901; steroids s. *8*, 181; s. a. P. L. Julian et al., Am. Soc. *77*, 4601 (1955)

o-Hydroxyethers from xanthydrols ←
s. *6*, 162

Hydrogen peroxide/potassium hydroxide H_2O_2/KOH

Oxidative ring opening C

1,2,3-Hydroxydiketones from ketones
s. *9*, 230

Hydrogen peroxide/ammonium molybdate H_2O_2/NH_4MoO_4
s. *8*, 182

Phthalides from naphthalene ring
s. *6*, 187

m-Xylenesulfonic acid RSO_3H

Blocking of carboxyl groups C:C → CHC(OCOR)
by formation of 2-tetrahydropyranyl esters
s. *8*, 839

Sulfoacetic acid $HO_3S{\cdot}CH_2COOH$

Enol acetates from ketones and ketene ←
s. *8*, 183

Sulfuric acid H_2SO_4

Ethers from ethylene derivatives C:C → CHC(OR)
s. *7*, 811; *9*, 231; tert-butyl aryl ethers s. D. R. Stevens, J. Org. Chem. *20*, 1233 (1955)

Acoxy compounds from ethylene derivatives C:C → CHC(OCOR)
s. *9*, 232

Carboxylic acid esters from ethylene derivatives
s. *7*, 212

Blocking of carboxyl groups
by formation of 2-tetrahydropyranyl esters
s. *8*, 839

Lactones from phenols ←
s. *8*, 184

Sulfuric acid/formic acid $H_2SO_4/HCOOH$

Hydration of ethylene derivatives C:C → CHC(OH)
s. *9*, 790

Chromic acid CrO_3

Oxidative ring opening C
s. *6*, 188

Furan ring opening
s. *6*, 189

Indole ring opening
s. *7*, 213

Tungstic acid WoO_3

Glycols from ethylene derivatives C:C → C(OH)C(OH)
cis-trans-Isomers s. *6*, 190

Halogen ←

2,5-Dialkoxy-2,5-dihydrofurans from furans ←
s. *7*, 214

Bromine *Br*

2,5-Diacoxy-2,5-dihydrofurans from furans ←
s. *7*, 215

Iodine/silver arylcarboxylate s. Silver arylcarboxylate/iodine *I/ArCOOAg*

Perchloric acid $HClO_4$

Acoxy compounds from ethylene derivatives C:C → CHC(OCOR)
s. *9*, 232

Periodic acid and periodate IO_4^-

Oxidative ring opening ↻
s. *7*, 873; carbohydrates s. J. Baddiley, J. G. Buchanan, and L. Szabó, Soc. *1954*, 3826

Aldehydocarboxylic acids
s. *7*, 216

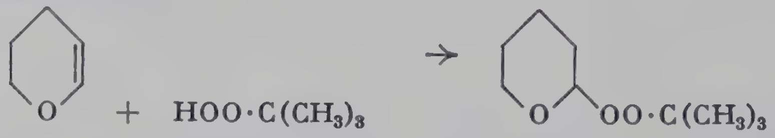
Hydrochloric acid *HCl*

2-Alkoxy-1,4-oxathianes from 1,4-oxathienes C:C → CHC(OR)
s. *7*, 880

β-Alkoxyacetals from α,β-ethylenealdehydes
s. *6*, 220

2-Tetrahydropyranyl peroxides from dihydropyrans C:C → CHC(OOR)

150.



A little ethereal HCl added to a soln. of *tert*-butyl hydroperoxide in dihydropyran, and allowed to stand 3-12 hrs. → *tert*-butyl tetrahydropyranyl peroxide. Y: 90-100%. F. e. s. J. Rigaudy and G. Izoret, C. r. *236*, 2086 (1953).

Carboxylic acid esters from keteneacetals $C{:}C(OR)_2 \rightarrow CHCOOR$
s. *8*, 185

Orthocarboxylic acid esters from keteneacetals $C{:}C(OR)_2 \rightarrow CHC(OR)_3$
s. *8*, 186

Hydrobromic acid *HBr*

2,3,5-Trialkoxytetrahydrofurans C:C → CHC(OR)
s. *9*, 234

Potassium permanganate $KMnO_4$

α-Diketones from acetylene derivatives C⋮C → COCO
s. *6*, 191

Oxidative ring opening ⊂

s. *4*, 175; s. a. A. L. Searles and R. M. Warren, J. Org. Chem. *18*, 1317 (1953)

Osmium tetroxide *OsO_4*

Pyrazine ring degradation

s. *6*, 41

Via intermediates *v.i*

Alcohols from ethylene derivatives via dihydrospiro-1,3-oxazines C:C → CHC(OH)

s. *8*, 413

Ketones from acetylene derivatives via enamines C⋮C → $COCH_2$

s. *7*, 217

1,2-Diacetals from enediolethers via 1,2-dialkoxy-1,2-dihalides ←

s. *7*, 218

Rearrangement

Hydrogen/Oxygen Type **OC ∩ HO**

Without additional reagents *w.a.r.*

Lactones from ethylenecarboxylic acids ○

s. *8*, 187

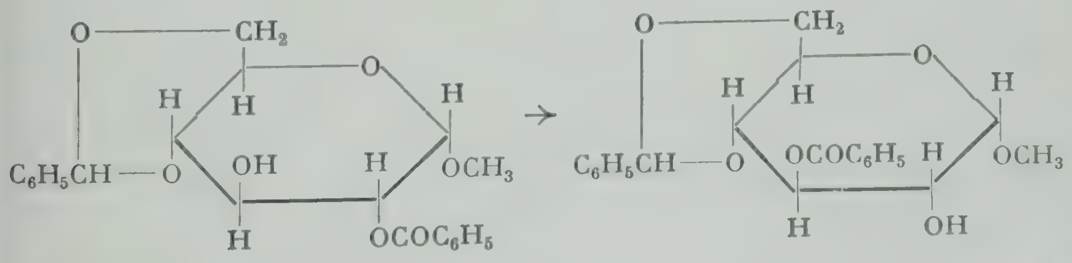
Alkali hydroxide ←

Smiles rearrangement ←

s. *9*, 235

Sodium hydroxide *NaOH*

Acyl migration in carbohydrates ←

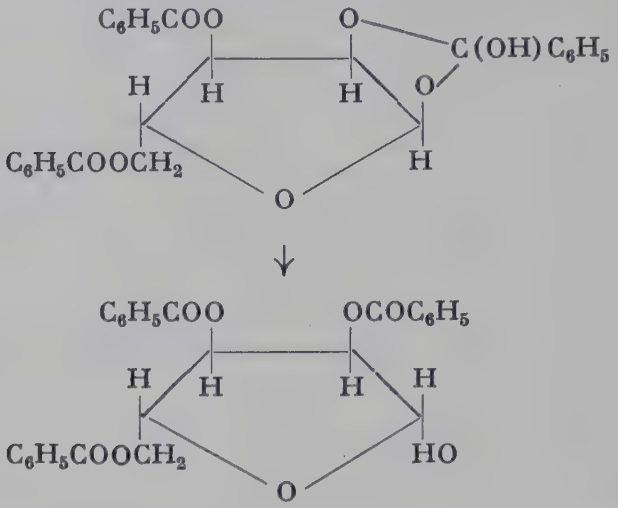


Approximately 0.05 *N* NaOH added to 0.086 g. methyl 2-benzoyl-4.6-benzylidene-α-D-glucoside in acetone → 0.056 g. methyl 3-benzoyl-4.6-benzylidene-α-D-glucoside.—The migration is normally directed away from the potential reducing group. E. J. Bourne, A. J. Huggard, and J. C. Tatlow, Soc. *1953*, 735.

Pyridine C_5H_5

Acylcarbohydrates from orthocarboxylic acid derivatives of carbohydrates ←

152.



A soln. of 3,5-di-O-benzoyl-1,2-O-(1-hydroxybenzylidene)-α-D-ribose i pyridine-water kept 31.5 hrs. at room temp. → 2,3,5-tri-O-benzoyl-β-D-ribose. Y: 65%. R. K. Ness and H. G. Fletcher, Jr., Am. Soc. *76*, 1663 (1954).

Thionyl chloride $SOCl_2$

Isomerization of dicarboxylic acid monoesters via dicarboxylic acid chloride esters ←

s. *8*, 188

Sulfuric acid H_2SO_4

Lactones from ethylenecarboxylic acids ○

s. *3*, 137; *8*, 189; by warming with 70%-H_2SO_4 to 45—55° s. K. W. Rosenmund und H. Herzberg, B. *87*, 1878 (1954)

Hydrogen fluoride HF

s. *7*, 219

Hydrochloric acid HCl

s. *8*, 190

Hydrogen/Carbon Type OC↶HC

Potassium hydroxide KOH

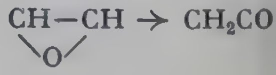
α-Diketones from chalcones via α,β-oxidoketones COCO

s. *6*, 192

Lithium diethylamide $(CH_3)_2NLi$

Ketones from oxido compounds

s. *8*, 191



$\underset{\diagdown O \diagup}{CH-CH} \rightarrow CH_2CO$

Boron fluoride BF_3

s. *8*, 192; *9*, 236

Isomerase

Aldoses from ketoses ←
←

53. An aq. soln. of commercial Ba-D-fructose-6-phosphate treated with an isomerase preparation, seed crystals added, and allowed to stand 16 hrs. at room temp. → Ba-D-glucose-6-phosphate heptahydrate. Y: 79%. —The equilibrium is displaced by the precipitation of the highly insoluble Ba-D-glucose-6-phosphate heptahydrate. W. A. Wood, Biochem. Prep. *3*, 71 (1953).

Formic acid $HCOOH$

Oxo compounds from glycol monoethers ←

s. *7*, 750

Titanium tetrachloride $TiCl_4$

α- from β-Glycosides ←

s. *6*, 193

Sulfur S

Willgerodt reaction ←

Carboxylic acid amides from oxido compounds

s. *9*, 237

Ammonium polysulfide $(NH_4)_2S_x$

Carboxylic acid amides from ketones

s. *1*, 151/2; *2*, 180/a; s. a. A. Dornow and G. Petsch, B. 86, 1404 (1953)

Sulfuric acid H_2SO_4

Oxo compounds from glycols $C(OH)CH(OH) \rightarrow CHCO$

s. *7*, 220

Ketones from glycol acetates $C(OAc)CH(OAc) \rightarrow CHCO$

s. *6*, 185

Pyridine hydrochloride C_5H_5N,HCl

Ketones from glycols $C(OH)CH(OH) \rightarrow CHCO$

s. *7*, 221

Hydrochloric acid HCl

Epimerization of steroids ←

s. *8*, 193

Ketones from glycols $C(OH)CH(OH) \rightarrow CHCO$

s. *8*, 194

Formation of α-ketoacetals with rearrangement ←

s. *9*, 238

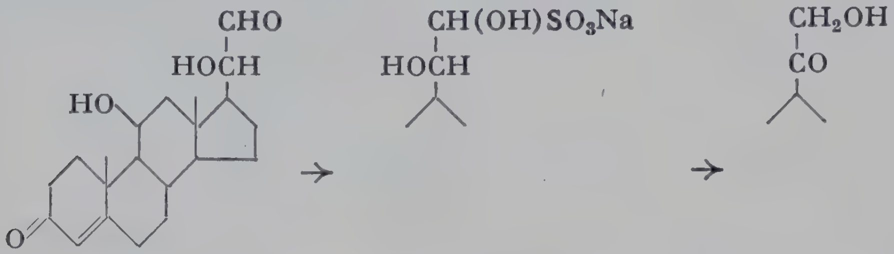
Hydrobromic acid *HBr*

α,β-Ethyleneketones ←
from oxidoalcohols via β-hydroxyketones
Partial dehydration
s. *9*, 239

Via intermediates *v.i.*

α-Hydroxyketones from α-hydroxyaldehydes ←
via α,β-dihydroxysulfonates

154.



Aq. $NaHSO_3$ added to crude Δ^4-pregnene-11β-20β-diol-3-one-21-al in methanol, and kept 1 hr. at 25° → Na-bisulfite addition compound (Y: 63%) in methanol treated under N_2 with freshly prepared methanolic Na-methoxide, and stirred 0.5 hr. at 22° → corticosterone (Y: 60%). D. Taub et al., Am. Soc. *76*, 4094 (1954).

Willgerodt-Kindler reaction $COCH_3 \rightarrow CH_2COOH$
s. *2*, 181; s. a. Am. Soc. *76*, 6196 (1954); H. Wolkowitz and M. S. Dunn, Biochem. Prep. *4*, 6 (1955)

Removal of sulfur
s. *9*, 240

Inversion of configuration via oxazolines ←
s. *5*, 154; s. a. A. Bolhofer, Am. Soc. *75*, 4469 (1953)

Oxygen/Oxygen Type OC↶OO

Acetic anhydride *$(CH_3CO)_2O$*

Rearrangement of N-heterocyclic ozonides ←
s. *9*, 241

Oxygen/Nitrogen Type OC↶ON

Without additional reagents *w.a.r.*

Beckmann rearrangement – Meisenheimer rule ←
s. *7*, 222

Potassium/alcohol *KOR*

Ethylenimines from oxime sulfonates ←
via Neber rearrangement intermediate
s. *9*, 242

Acetic anhydride *$(CH_3CO)_2O$*

N-Heterocyclic carbinols and aldehydes via N-oxides ←

s. *9*, 243

Polyphosphoric acid *$H(PO_3H)_xOH$*

Beckmann rearrangement ←

Carboxylic acid amides and lactams (ring expansion) from oximes

s. *7*, 224; acylamines s. E. R. Ward and T. M. Coulson, Soc. *1954*, 4545

Benzenesulfonyl chloride *$C_6H_5SO_2Cl$*

Amines from ketones via oximes

s. *8*, 195

Ring opening ↺

Cyanocarboxylic acids from phenols via α-isonitrosoketones

s. *7*, 223; s. a. Am. Soc. *77*, 670 (1955)

p-Acetylaminobenzenesulfonyl chloride ←

Lactams from oximes – Ring expansion – Steroids ←

s. *8*, 196

Sulfuric acid *H_2SO_4*

Beckmann rearrangement ←

Acylamines from oximes

s. *8*, 197

Ring expansion

s. *4*, 182; isomeric lactams s. A. Schäffler and W. Ziegenbein, B. *88*, 1374 (1955)

Hydroxyazo from azoxy compounds ←

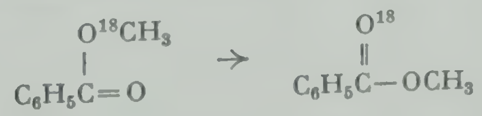
Wallach transformation

s. *9*, 244

Oxygen/Carbon Type **OC↶OC**

Without additional reagents *w.a.r.*

Thermal rearrangement of carboxylic acid esters ←



$$C_6H_5C(=O)O^{18}CH_3 \rightarrow C_6H_5C(=O^{18})-OCH_3$$

O^{18}-Ether labeled methyl benzoate heated 3 hrs. at 400-405° in a sealed tube under N_2 → O^{18}-carbonyl labeled methyl benzoate. Conversion 66% determined with mass spectrometer. K. B. Wiberg, Am. Soc. *75*, 2665 (1953).

Acetic acid CH_3COOH

Oxazoline ring ○
s. *6*, 194

Perchloric acid $HClO_4$

Ketones from oxido compounds with rearrangement ←
s. *9*, 227

Hydrochloric acid *HCl*

Acylglycosides ←
from orthocarboxylic acid derivatives of carbohydrates
s. *8*, 198

Nitrogen/Carbon Type OC↶∩NC

Without additional reagents *w.a.r.*

Aminoethers from quaternary hydroxyammonium salts ←
s. *8*, 199

Aminocarboxylic acid esters from betaines ←
s. *6*, 222

(tert-Amino)enolethers from quaternary ketoammonium salts ←
s. *8*, 200

Alkoxylamines from amines via N-oxides ←
s. *7*, 225

O-Alkoximes from N-alkoximes ←
s. *7*, 226

Ring expansion ←
  Alkoximes from nitrones – Oxazine from pyrrole ring
  s. *7*, 227

  1,2-Oxazines from pyrrole N-oxides
  s. *6*, 195

Sodium/alcohol *NaOR*

Oxazoles and hydantoins from α-ureidonitriles ○
s. *9*, 245

Thionyl chloride $SOCl_2$

O-Acyl from N-acyl via oxazolines NAc → OAc
s. *6*, 196

Hydrochloric acid *HCl*

Acyl group migration NAc → OAc
as used for determination of configuration
s. *9*, 246; s. a. S. P. Findlay, Am. Soc. *76*, 2855 (1954); migration s. a. A. Dornow and H. Theidel, B. *88*, 1267 (1955)

Oxazoles from α-acylaminonitriles ○
s. *6*, 197

1,3-Oxathiole ring from hydroxythiocyanates
s. *8*, 201

α-Aminoketones from 2-alkoxyethylenimines ⊂
s. *9*, 247

Oxazolidine ring opening with acyl migration
O-Acyl from N-acyl s. *8*, 35

Sulfur/Carbon Type OC∩SC

s. *9*, 248

Carbon/Carbon Type OC∩CC

Without additional reagents *w.a.r.*

m-Dioxane ring ○
s. *6*, 198

Alkali hydroxide ←

α-Hydroxycarboxylic acids from o-quinones ←
Benzilic acid-type rearrangement
Ring contraction of isocyclics
with KOH s. *7*, 228; with NaOH s. N. Greenhalgh, Soc. *1954*, 4699

Sodium hydroxide $NaOH$

Ketones from 2-ethylenealcohols C:C·C(OH) → CHCH·CO
Steroids
s. *8*, 202

Zinc Zn

s. *10*, 90

Zinc chloride $ZnCl_2$

Coumarans ○
s. *8*, 203

Mercuric chloride $HgCl_2$

Furans from acetyleneglycols
s. *9*, 249

Boron fluoride/mercuric oxide/trichloroacetic acid $BF_3/HgO/CCl_3COOH$

Pyrone ring
s. *7*, 229

Acetic acid CH_3COOH

Chromono(3′,2′,3,4)coumarin ring
s. *6*, 199

Sulfuric acid H_2SO_4

α,β-Ethylenecarboxylic acid esters ←
from alkoxyacetylenealcohols
s. *6*, 200; s. a. E. A. Braude and O. H. Wheeler, Soc. *1955*, 320

Tetrahydrofuranones, dihydrofurans, ←
and α-diketones from acetylenediols
s. *7*, 230

Hydrochloric acid — *HCl*

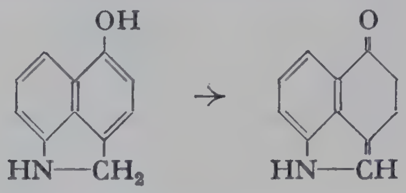
Ketones from 2-ethylenealcohols — C:C·C(OH) → CHCH·CO
Steroids s. *8*, 202

4-Pyrones — ○
s. *7*, 231

Palladium-carbon — *Pd-C*

Cyclic ketones from phenols by isomerization ←

156.



Powdered 5-hydroxybenz[cd]indoline added portionwise during 2-2.5 hrs. in a H_2-stream to a Pd-Norit catalyst (prepn. s. original) in tetralin-xylene, and the product isolated after 8 hrs. in the H_2-stream → 5-oxo-1,3,4,5-tetrahydrobenz[cd]indole. Y: 90%.—In the absence of H, dehydrogenation to 5-oxo-1,5-dihydrobenz[cd]indole takes place. C. A. Grob and B. Hofer, Helv. *35*, 2095 (1952).

Ketoindoles from hydroxybenz[cd]indolines ←
s. *7*, 232

Exchange

Hydrogen ↑ — OC⇅H

Nitrobenzene/chromic acid s. Chromic acid/nitrobenzene — $C_6H_5NO_2/CrO_3$

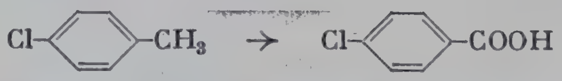
Lead tetraacetate — $(CH_3COO)_4Pb$

Furanones from furans ←
s. *9*, 250

Nitric acid — HNO_3

Oxidation of side chains — R → COOH

157.



can be achieved with dil. HNO_3 at 200° and 30-50 atm. pressure. The crude acids are somewhat contaminated with nitrated products.—E: p-Chlorotoluene allowed to react with 30% excess 15%-HNO_3 at 180°/28 atm. → crude chlorobenzoic acid. Y: 87%. F. e. s. E. B. Bengtsson, Acta Chem. Scand. *7*, 774 (1953); *8*, 842 (1954); *9*, 832 (1955).

Oxidation of methyl groups ←
Lactones from hydroxy compounds
s. *10*, 130

Carboxylic acids

from alcohols $CH_2OH \rightarrow COOH$
s. *7*, 233

from formoxy compounds $CH_2OCHO \rightarrow COOH$
s. *10*, 229

Nitric acid/sodium nitrite $HNO_3/NaNO_2$
Carboxylic acids from alcohols $CH_2OH \rightarrow COOH$
s. *6*, 170

Oxygen/potassium hydroxide O_2/KOH
Ketones from hydrocarbons $CH_2 \rightarrow CO$
s. *7*, 234

Hydrogen peroxide H_2O_2
Peroxycarboxylic acids from aldehydes $CHO \rightarrow COO_2H$
s. *7*, 241

Hydrogen peroxide/osmium tetroxide H_2O_2/OsO_4
s. Osmium tetroxide/hydrogen peroxide

Oxidations with
Potassium nitrosodisulfonate $ON(SO_3K)_2$
Quinones from phenols ←
s. *8*, 206

Potassium persulfate $K_2S_2O_8$
o-Aminosulfuric acid esters from ar. amines $H \rightarrow OSO_3K$
s. *9*, 203

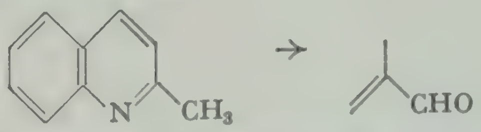
Selenium dioxide SeO_2
Aldehyde from methyl groups $CH_3 \rightarrow CHO$
s. *7*, 241

α-Ketocarboxylic acid esters from carboxylic acid esters $CH_2 \rightarrow CO$
Acylcyanides from nitriles
s. *7*, 235

1,2,3-Hydroxydiketones from ketones ←
s. *9*, 230

Carboxylic acid from methyl groups $CH_3 \rightarrow COOH$
s. *7*, 236

Molybdenum trioxide-silica $MoO_3\text{-}SiO_2$
Aldehyde from methyl groups $CH_3 \rightarrow CHO$



in the vapor phase. A mixture of quinaldine, water, and air passed at 410° passed through a 10%-MoO_3-on-silica catalyst → quinoline-2-aldehyde. Conversion: 40-60%; Y: 40-50%. F. e. s. W. Mathes and W. Sauermilch, B. *87*, 1179 (1954).

Sodium dichromate/acetic acid $Na_2Cr_2O_7/CH_3COOH$

Quinones from hydrocarbons ←
s. *3*, 151; in the presence of Ce-salts s. Org. Synth., Coll. Vol. III, 1 (1955)

Chromic acid CrO_3

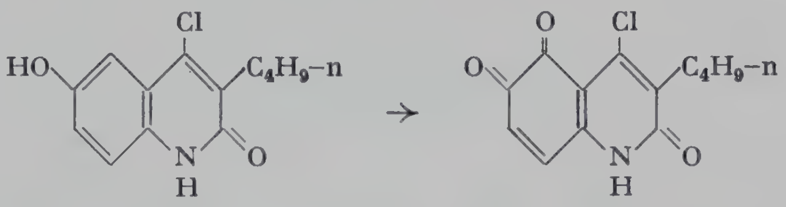
Aldehyde from methyl groups
via 1,1-diacoxy compounds CH_3 → CHO
s. *9*, 251

Ketones from hydrocarbons
with protection of hydroxyl groups CH_2 → CO
s. *8*, 207

5,7,12,14-Tetraazapentacene-6,13-quinones
from 5,12-dihydro-5,7,12,14-tetraazapentacenes ←
s. *8*, 556

o-Quinones from phenols ←
Carbostyril-5,6-quinones from 6-hydroxycarbostyrils

159.



3-n-Butyl-4-chloro-6-hydroxycarbostyril dissolved with warming in glacial acetic acid, water and H_2SO_4 added, cooled below room temp., aq. CrO_3 added dropwise during 1-2 min. with stirring which is continued for 0.5 hr. → 3-n-butyl-4-chlorocarbostyril-5,6-quinone. Y: 83%. F. e. s. R. R. Holmes et al., Am. Soc. *76*, 2400 (1954).

Carboxylic acid from methyl groups CH_3 → COOH
s. *9*, 252

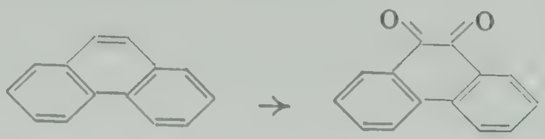
Carboxylic acids from alcohols CH_2OH → COOH
s. *6*, 233

Oxidation of 3-arylfurans ←
s. *9*, 253

Chromic acid/nitrobenzene $CrO_3/C_6H_5NO_2$

Quinones from hydrocarbons ←
s. *9*, 254

Chromic acid/sulfuric acid CrO_3/H_2SO_4



Concd. H_2SO_4 followed by aq. CrO_3 added to a mixture of technical grade phenanthrene and aq. CrO_3 in such a manner that violent boiling is avoided, finally refluxed 20 min. → phenanthrenequinone. Y: 44-48%. R. Wendland and J. LaLonde, Org. Synth. *34*, 76 (1954).

tert-Butyl chromate ←

α,β-Ethyleneketones from ethylene derivatives $CH_2 \rightarrow CO$

s. *8*, 208

Chromyl chloride CrO_2Cl_2

Aldehyde from methyl groups $CH_3 \rightarrow CHO$

s. *8*, 209

tert-Butyl hypochlorite $(CH_3)_3C{\cdot}OCl$

Carboxylic acid esters from 2 alcohol molecules $2\,RCH_2OH \rightarrow RCOOCH_2R$

s. *9*, 363

Hydrobromic acid HBr

Oxidation of hydrocarbons ←

Ketones and hydroperoxides from hydrocarbons

s. *6*, 201

Manganese dioxide MnO_2

Oxo compounds from hydrocarbons $CH_2 \rightarrow CO$

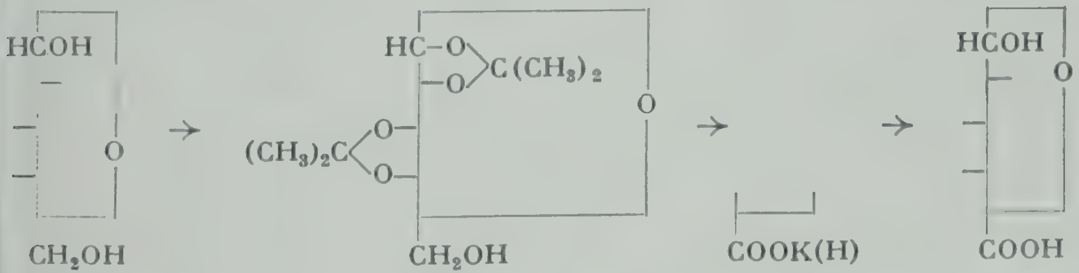
s. *8*, 210

Potassium permanganate $KMnO_4$

Ketones from hydrocarbons

s. *6*, 202

Uronic acids from carbohydrates via isopropylidene derivatives $CH_2OH \rightarrow COOH$



A mixture of anhydrous D-galactose, anhydrous $CuSO_4$, concd. H_2SO_4, and acetone shaken 24 hrs., filtered, the filtrate shaken with powdered

$Ca(OH)_2$ until neutral to Congo red, then the product isolated → crude diacetone-D-galactose (Y: 76-92%) in aq. KOH stirred and treated portionwise with $KMnO_4$ over a period of 5 hrs., and the product isolated after stirring for 24 hrs. → K-salt of diacetone-D-galacturonic acid (Y: 49-65%) dissolved in 0.5 *N* H_2SO_4 and extracted with ether → diacetone-D-galacturonic acid (Y: 78-88%) heated 2 hrs. with water on a water bath → D-galacturonic acid monohydrate (Y: 65-81%). K. P. Link and H. M. Sell, Biochem. Prep. *3*, 74 (1953).

α-Ketocarboxylic acids from methyl ketones $COCH_3 \rightarrow COCOOH$
s. *6*, 203; *10*, 195

Potassium permanganate/pyridine $KMnO_4/C_5H_5N$

Carboxylic acid from methyl groups $CH_3 \rightarrow COOH$
s. *9*, 255

Ferric oxide-alumina Fe_2O_3-Al_2O_3

s. *8*, 211

Ferric chloride $FeCl_3$

α-Diketones from ketones $COCH_2 \rightarrow COCO$
s. *7*, 237

Potassium ferricyanide $K_3[Fe(CN)_6]$

α-Oxo-N-heterocyclics ←
from cyclic quaternary ammonium salts
from halides s. *2*, 264; *3*, 226; from tosylates s. C. F. Koelsch and A. F. Steinhauer, J. Org. Chem. *18*, 1516 (1953)

Osmium tetroxide/hydrogen peroxide OsO_4/H_2O_2

α-Hydroxyketones from ethylene derivatives $C{:}CH \rightarrow C(OH)CO$
s. *7*, 238

Platinum and platinum-carbon *Pt and Pt-C*

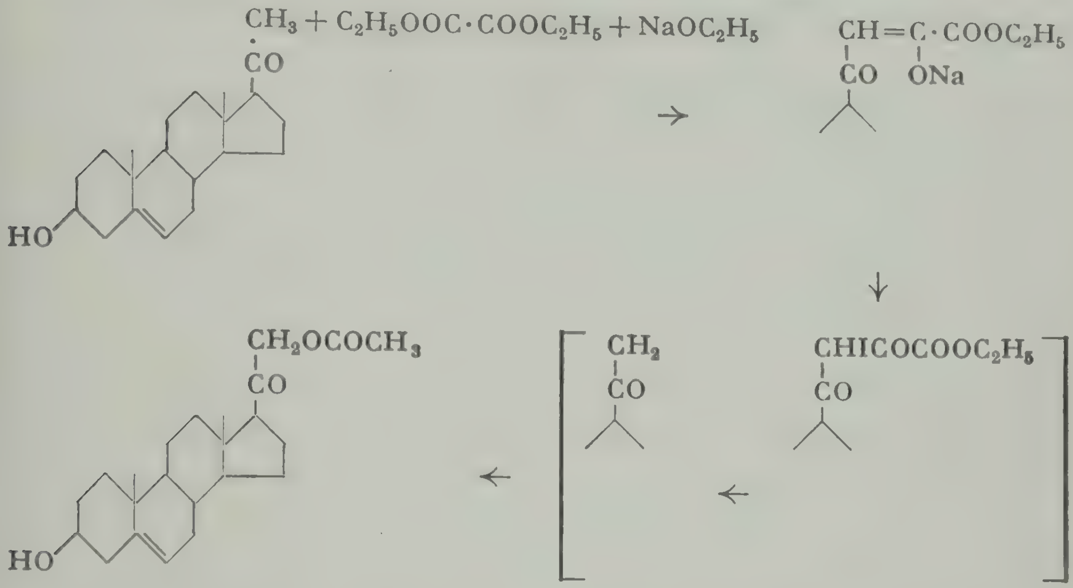
Catalytic oxidation $CH_2OH \rightarrow COOH$
Carboxylic acids from alcohols
s. *8*, 212; s. a. K. Heyns and H. Paulsen, B. *88*, 188 (1955)

Via intermediates *v.i.*

Acoxy-2-ethylenes from ethylene derivatives ←
via glycol monoesters
s. *7*, 239

α-Acetoxyketones from ketones via α,γ-diketocarboxylic acid esters, β-iodo-α,γ-diketocarboxylic acid esters, and α-iodoketones

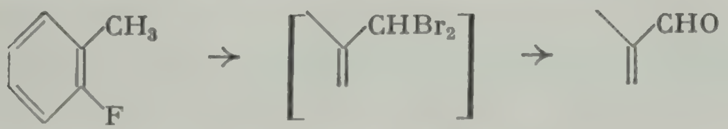
H → OAc



5-Pregnen-3β-ol-20-one dissolved in a warm soln. of Na in ethanol, then ethyl oxalate in ethanol added, refluxed 6 hrs., and allowed to stand overnight → Na salt of ethyl 5-pregnen-3β-ol-20-onyl-21-glyoxylate (Y: 95%) suspended in abs. methanol, a soln. of iodine in methanol added with stirring at –15° during 15 min., after an additional 0.5 hr. a soln. of Na in methanol added slowly, stirred 1 hr., water added during 1 hr. and the resulting moist 21-iodo-5-pregnen-3β-ol-20-one refluxed 5 hrs. with K-acetate in acetone-water-acetic acid → 21-acetoxy-5-pregnen-3β-ol-20-one. Y: 74%. H. Ruschig, B. *88*, 878 (1955).

Aldehyde from methyl groups via 1,1-dibromides

CH_3 → CHO



o-Fluorotoluene irradiated with a 300 W lamp and treated with Br at 105-110° for 1 hr., then at 110-135° for 2 more hrs., finally the temp. raised to 150° for 10-15 min., and the crude product refluxed 14-16 hrs. with $CaCO_3$ in water → o-fluorobenzaldehyde. Y: 70-76%. V. V. Korshak and G. S. Kolesnikov, Sint. Org. *2*, 140 (1952); C. A. *48*, 636i; bromination s. a. E. L. Eliel and K. W. Nelson, Soc. *1955*, 1628.

Coumarandiones from coumaran-3-ones via 2-oximinocoumaran-3-ones

CH_2 → CO

s. *8*, 214

α,β-Ethyleneketones from ethylene derivatives via α-nitrosohalides and α,β-ethyleneoximes ←
s. *7*, 240

Quinones from hydrocarbons via quinols ←
s. *9*, 256

Carboxylic acid from methyl groups $CH_3 \rightarrow COOH$
via ethylene derivatives
s. *6*, 135

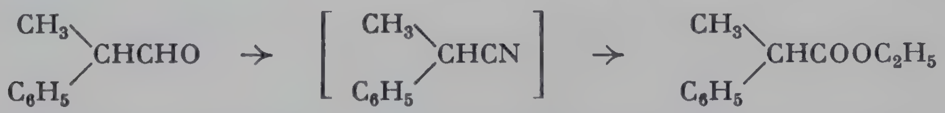
via aldehydes and peroxycarboxylic acids
s. *7*, 241

via trichlorides
s. *8*, 213

Carboxylic acids from alcohols via aldehydes $CH_2OH \rightarrow COOH$
s. *6*, 292

Carboxylic acid esters from aldehydes via nitriles $CHO \rightarrow COOR$

164.



$$\begin{matrix}CH_3\\ \quad CHCHO\\ C_6H_5\end{matrix} \rightarrow \left[\begin{matrix}CH_3\\ \quad CHCN\\ C_6H_5\end{matrix}\right] \rightarrow \begin{matrix}CH_3\\ \quad CHCOOC_2H_5\\ C_6H_5\end{matrix}$$

A soln. of HCl in 95%-ethanol satd. at 0-5° mixed with hydratropic aldehyde, NaN_3 added in small portions with stirring and cooling, after 3 hrs. allowed to warm to room temp., then refluxed gently for 4 hrs. → ethyl hydratropate. Y: 51%. P. A. S. Smith, D. R. Baer, and S. N. Ege, Am. Soc. *76*, 4564 (1954).

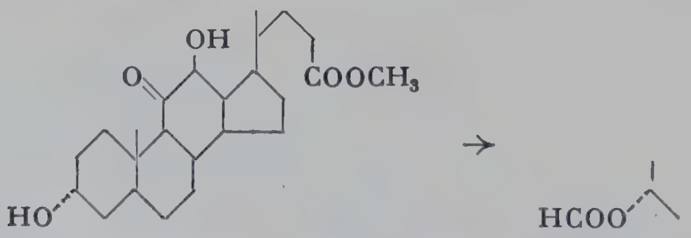
Oxygen ↑ OC⇵O

Without additional reagents *w.a.r.*

Acylation of alcohols OH → OAc
s. *7*, 550

Formoxy compounds – Partial O-acylation OH → OCHO

165.



A soln. of methyl 3α,12β-dihydroxy-11-ketocholanate in 90%-formic acid heated to 65°, then allowed to stand for 3 hrs. → methyl 3α-formoxy-12β-hydroxy-11-ketocholanate. Y: 91.5%. F. e. s. S. Archer et al., Am. Soc. *76*, 4915 (1954).
s. a. *8*, 215

Mild acetylation OH → OAc
s. *7*, 242

Carboxylic acid esters from carboxylic acid anhydrides $(RCO)_2O \rightarrow RCOOR'$
s. *9*, 257

Dicarboxylic acid monoesters ←

166. $HOOC[CF_2]_4COOH + C_2H_5OOC[CF_2]_4COOC_2H_5 \rightarrow HOOC(CF_2]_4COOC_2H_5$

Anhydrous perfluoroadipic acid and ethyl perfluoroadipate heated 3 hrs. at 170° → ethyl hydrogen perfluoroadipate. Y: 80%. W. H. Rauscher and H. Tucker, Am. Soc. *76*, 3599 (1954).

Acyloximes :NOH → :NOAc
s. *7*, 161

Acoxysilanes from silanols SiOH → SiOAc
s. *8*, 216

Potassium/nickel-silica s. Nickel-silica/potassium *K/Ni-SiO$_2$*

Sodium hydroxide *NaOH*

Ethers from p-toluenesulfonic acid esters OTs → OR
s. *8*, 660

Acoxycarboxylic acids from hydroxycarboxylic acids OH → OAc
s. *8*, 217

Potassium hydroxide *KOH*

Nitronates $:\mathrm{N}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OR}\end{smallmatrix}$
s. *6*, 204

Sodium alkoxide *NaOR*

Ethers from p-toluenesulfonic acid esters OTs → OR
s. *8*, 660

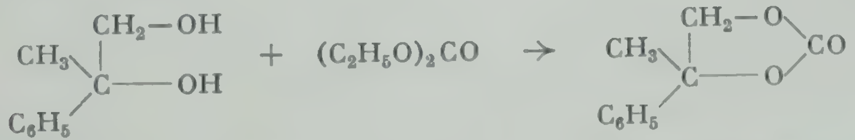
Methyllithium *CH$_3$Li*

Acylation of slow reacting hydroxyl groups OH → OAc
Selective acylation of phenol groups
s. *9*, 258

Potassium carbonate *K$_2$CO$_3$*

1,3-Dioxolan-2-ones ○

167.



A soln. of 2-phenyl-1,2-propanediol, 10% excess diethyl carbonate, and a small amount of K-carbonate in benzene gently refluxed for 3 hrs. into a small packed column whereby a distillate, b. p. near 67°, is collected → 4-methyl-4-phenyl-1,3-dioxolan-2-one. Y: 93%. M. S. Newman, W. M. Edwards and R. Addor, Am. Soc. *76*, 1840 (1954); cf. H. Najer, P. Chabrier, and R. Guidicelli, Bl. *1954*, 1142

Sodium acetate CH_3COONa

Acetylation OH → OAc

s. *2*, 193; *3*, 158; s. a. B. B. Schaeffer, M. C. Blaich, and I. W. Churchill, J. Org. Chem. *19*, 1646 (1954); C. G. Overberger and D. Tanner, Am. Soc. *77*, 369 (1955)

with simultaneous formation of lactones from hydroxycarboxylic acids
s. *8*, 328

Enolesters from aldehydes CHCHO → C:CH(OAc)
s. *6*, 214

Diene synthesis via enolesters
s. *6*, 695

Potassium acetate CH_3COOK

Acylation ←
with formation of a naphthalene from an indole ring
by migration of a carbon-carbon double bond
Phenol acetates from cyclic ketones
s. *10*, 311

Enolesters from aldehydes CHCHO → C:CH(OAc)
s. *6*, 575

Potassium salt K^+

α-Ketocarboxylic acid ester enolesters C:C(OAc)COOR
s. *7*, 774

Ammonia NH_3

6-Alkoxy-5,6-dihydrophenanthridines OH → OR
s. *6*, 820

Ammonium and amine salts ←

Esterification of acid sensitive compounds RCOOR′
s. *9*, 259

Triethylamine $(C_2H_5)_3N$

Carboxylic acid esters from carboxylic acids via mixed carboxylic acid anhydrides COOH → COOR
s. *9*, 453

Pyridine C_5H_5N

Formoxy compounds OH → OCHO
s. *9*, 17

Acetylation OH → OAc
s. *10*, 224, 243

of optically active alcohols
s. *7*, 579

Total acetylation of aminosugars
s. *10*, 297

Selective acetylation
of sec. hydroxyl groups
s. *6*, 206
of phenol groups
s. *9*, 258

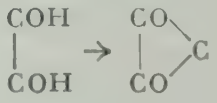
Unsatd. esters of sucrose $OH \rightarrow OCOCH{:}CHCH_3$
s. *6*, 205

Enolesters $C{:}CH(OAc)$
s. *6*, 207

from ketones
with migration of carbon-carbon double bond
s. *8*, 218

Cupric sulfate/sulfuric acid $CuSO_4/H_2SO_4$

Isopropylidene derivatives of carbohydrates
s. *10*, 161



Zinc chloride (s. a. under P_2O_5 and H_3PO_4) $ZnCl_2$

Acetals – Carbohydrate derivatives
s. *2*, 200; s. a. G. R. Baker et al., Soc. *1955*, 1327

m-Dioxanes
s. *8*, 219

Bauxite Al_2O_3

Carboxylic acid esters from carboxylic acids $COOH \rightarrow COOR$
s. *6*, 420

Boron fluoride BF_3

α-Halogenoglycol monoethers from α-halogenoglycols $OH \rightarrow OR$
s. *8*, 220

Carboxylic acid esters from carboxylic acids $COOH \rightarrow COOR$
s. *6*, 209

Lactolesters from lactols ←
s. *9*, 272

Aluminum chloride $AlCl_3$

Enolethers $CHCO \rightarrow C{:}C(OR)$
s. *9*, 260

Methoxyacetylene $HC{\vdots}C{\cdot}OCH_3$

Acid anhydrides ←
s. *9*, 261

Acetic anhydride $(CH_3CO)_2O$

Carboxylic acid esters from carboxylic acids $COOH \rightarrow COOR$
s. *6*, 210

Trifluoroacetic anhydride $(CF_3CO)_2O$

Acylation of hydroxy compounds
s. *6*, 211; sterically hindered esters s. R. Reed, Jr., Am. Soc. 77, 3403 (1955)

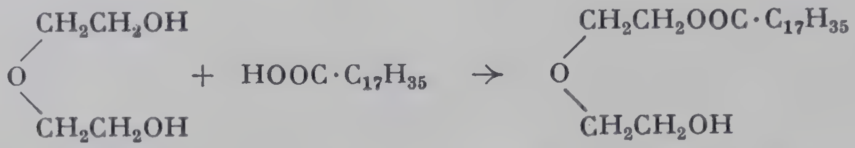
Cation exchange resin ←

Uronosides, glycosides, and isopropylidene derivatives of carbohydrates ←

s. 7, 243; glycosides s. a. D. F. Mowery, Jr., Am. Soc. 77, 1667 (1955)

Partial O-acylation OH → OCOR

168.



Azeotropic water entrainment. Stearic acid refluxed 18 hrs. with 12 moles diethylene glycol in toluene in the presence of Amberlite IR-120 at a bath temp. of 150° with separation of the water formed → diethylene glycol monostearate. Y: ca. 100%. F. e. s. M. J. Astle, B. Schaeffer, and C. O. Obenland, Am. Soc. 77, 3643 (1955).

Trifluoroacetic acid *CF_3COOH*

Acylation of alcohols OH →OAc

s. 7, 244

Methyl iodide *CH_3I*

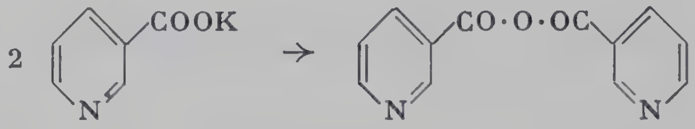
Ketals with simultaneous formation of sulfonium salts ←

s. 6, 212

Oxalyl chloride *$(COCl)_2$*

Carboxylic acid anhydrides from carboxylic acids 2 COOH → CO·O·OC

169.



0.5 mole oxalyl chloride in anhydrous benzene added with stirring and ice-cooling during 20 min. to a suspension of K-nicotinate in the same solvent, the cooling bath removed after another 15 min., stirred 1 hr. at room temp. and another hr. at reflux temp. → nicotinic anhydride. Y: 85%. F. e. s. A. W. Schrecker and P. B. Maury, Am. Soc. 76, 5803 (1954).

Ammonium nitrate *NH_4NO_3*

α,β-Ethyleneacetals from α,β-ethylenealdehydes CHO → $CH(OR)_2$

s. 6, 220

Phosphorus pentoxide *P_2O_5*

Carboxylic acid esters from carboxylic acids COOH → COOR

s. 6, 213

Phosphorus pentoxide/zinc chloride *$P_2O_5/ZnCl_2$*

Di- from mono-saccharides ←

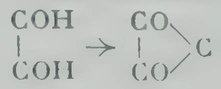
s. 8, 221

Phosphoric acid *H_3PO_4*

Sym. ethers from alcohols 2 ROH → ROR
s. *8*, 222

Phosphoric acid/zinc chloride *$H_3PO_4/ZnCl_2$*

Isopropylidene derivatives of carbohydrates
s. *7*, 245



$$\begin{matrix}\text{COH}\\ |\\ \text{COH}\end{matrix} \rightarrow \begin{matrix}\text{CO}\\ |\\ \text{CO}\end{matrix}\!\!>\!\text{C}$$

Phosporus trichloride *PCl_3*

Acylation of alcohols OH → OAc
α-Formoxyketones from α-hydroxyketones
s. *9*, 262

Phosphorus oxychloride *$POCl_3$*

Carboxylic acid phenolesters COOH → COOR
s. *8*, 223

Ozone *O_3*

Ketones from aldehydes via enolesters ←
Degradation with loss of 1 C-atom
s. *6*, 214

Thionyl chloride *$SOCl_2$*

Acylation of alcohols OH → OAc
α-Formoxyketones from α-hydroxyketones
s. *9*, 262

Carboxylic acid esters from carboxylic acids COOH → COOR
s. *9*, 344; s. a. R. A. Boissonnas et al., Helv. *38*, 1491 (1955); A. F. Olechnowitz and G. Zimmermann, Ang. Chem. *67*, 209 (1955)

Thionyl chloride/sodium alkoxide *$SOCl_2/NaOR$*
s. *9*, 263

p-Toluenesulfonyl chloride *TsCl*

Ethers ROR
s. *8*, 224

p-Toluenesulfonic acid *TsOH*
s. *9*, 264

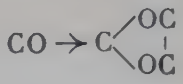
Enolethers C:C(OR)
s. *6*, 215; *7*, 150

α-Alkoxymethylene from α-hydroxymethylene compounds :CHOH → :CHOR
s. *7*, 118

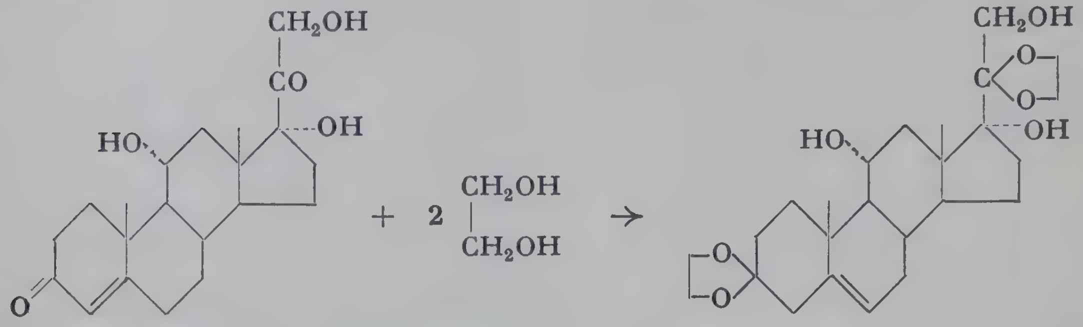
α,β-Ethyleneacetals from α,β-ethylenealdehydes CHO → $CH(OR)_2$
s. *9*, 265

α-Ketoacetals from α-hydroxymethyleneketones ←
s. *9*, 266

Ketals



170.



A mixture of 11-*epi*-hydrocortisone, a large excess of ethylene glycol, and a little p-toluenesulfonic acid monohydrate stirred and slowly distilled at ca. 80°/2 mm. over a period of 5 hrs. → 11-*epi*-hydrocortisone bis-ethylene ketal. Y: 76%.—In certain cases, this procedure gives higher yields than azeotropic distillation with benzene. F. e. s. W. S. Allen, S. Bernstein, and R. Littell, Am. Soc. *76*, 6116 (1954).

β-Hydroxyketones from β-ketocarboxylic acid esters
Blocking of keto groups by formation of alkylene ketals
s. *6*, 216

Acetylation of alcohols OH → OAc
by azeotropic distillation s. *6*, 217
11β-Acetoxysteroids s. *9*, 267

Carboxylic acid esters from carboxylic acids COOH → COOR
Azeotropic water separation
in chloroform s. *7*, 246; in benzene s. N. L. Drake and W. B. Tuemmler, Am. Soc. *77*, 1204 (1955)

Enolesters from ketones CHCO → C:C(OAc)
s. *7*, 184

1,3-Dioxolanes ○
s. *8*, 225

Sulfosalicylic acid ←

Acetylation of alcohols ←
with simultaneous formation of enolesters from ketones
s. *9*, 268

Sulfuric acid H_2SO_4

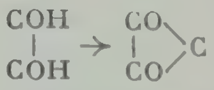
Ethers from alcohols via carbonium ions ROR
s. *4*, 201; s. a. Am. Soc. *77*, 1778 (1955)

Alkoxyhalides from halogenhydrins
s. *9*, 269

α-Aminoalcohols from cyanohydrins ←
with protection of the hydroxyl group
by formation of alkoxymethyl ethers
s. *9*, 270

Enolethers from ketones ←
with migration of a carbon-carbon double bond
s. *7*, 150

Ethylidene derivatives of carbohydrates
s. *9*, 355


$$\begin{matrix} COH \\ | \\ COH \end{matrix} \rightarrow \begin{matrix} CO \diagdown \\ | \quad\;\; C \\ CO \diagup \end{matrix}$$

Acetals from orthoformic acid esters $CO \rightarrow C(OR)_2$
s. *9*, 743; s. a. R. G. Jones, Am. Soc. *77*, 4074 (1955)

Acoxy- from hydroxy-mercaptans $OH \rightarrow OAc$
s. *9*, 271

Cyanohydrin acetates from cyanohydrins $C(CN)OH \rightarrow C(CN)OAc$
s. *8*, 717

Carboxylic acid esters from carboxylic acids $COOH \rightarrow COOR$
s. *7*, 827; *9*, 434

by azeotropic distillation
s. *6*, 218

Carboxylic acid β-chloroethyl esters
s. *8*, 226

Unsym. peroxides from hydroperoxides $R{\cdot}OOH \rightarrow R{\cdot}OO{\cdot}R'$
s. *7*, 247

Chlorosulfonic acid $ClSO_3H$

Carboxylic acid esters from carboxylic acids ←
Dicarboxylic acid esters from carboxylic acid anhydrides
Acylation of polyalcohols
s. *8*, 227

Perchloric acid $HClO_4$

Acetylation of carbohydrates $OH \rightarrow OAc$
Acetobromosugars
s. *6*, 582

Enolesters from ketones $CHCO \rightarrow C{:}C(OAc)$
s. *9*, 202

Lactolesters from lactols ←
s. *9*, 272

Unsym. peroxides from hydroperoxides $R{\cdot}OOH \rightarrow R{\cdot}OO{\cdot}R'$
s. *7*, 248

Hydrochloric acid HCl

Ethers from alcohols $ROH \rightarrow ROR'$
s. *7*, 191

Alkoxymethylureas from di(ureidomethyl) ethers ←
s. *9*, 273; s. a. M. *85*, 1196 (1954)

Protection of keto groups by formation of enolethers and ketals ←
s. *8*, 725

Acetals from orthoformic acid esters $CO \rightarrow C(OR)_2$
s. *6*, 219; *8*, 133

α,β-Ethyleneacetals and β-alkoxyacetals from α,β-ethylenealdehydes ←
s. *6*, 220

β-Ketoacetals from ketones via α-hydroxymethyleneketones ←
s. *9*, 816

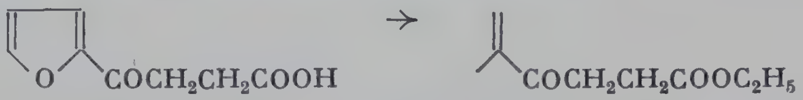
Lactolides from lactols OH → OR
s. *9*, 596

O-Acetylation OH → OAc
s. *8*, 228

Acetylation of hydroxy compounds
s. *9*, 791

Carboxylic acid esters from carboxylic acids COOH → COOR

171.



at room temp. β-Furfuroylpropionic acid dissolved in abs.-ethanolic HCl, and allowed to stand 12 hrs. at room temp. → ethyl β-furfuroylpropionate. Y: 96%. F. e. s. W. Gruber, B. *88*, 178 (1955); s. a. N. L. Drake and W. B. Tuemmler, Am. Soc. *77*, 1204 (1955); F. Bergel, V. C. E. Burnop, and A. Stock, Soc. *1955*, 1223.

Siloxane derivatives
s. *9*, 274

Peptide esters via peptide ester hydrochlorides
s. *8*, 230

Isomeric dicarboxylic acid monoesters
Partial esterification and hydrolysis
s. *8*, 229

γ-Carbalkoxy-α-aminocarboxylic acids from α-amino-γ-dicarboxylic acids
s. *8*, 231

Esterification with simultaneous dehydration
s. *6*, 689

1,1-Diperoxides from hydroperoxides ←
s. *7*, 249

Nickel-silica/potassium *Ni-SiO₂/K*

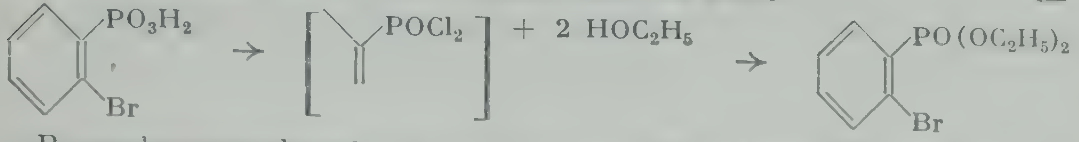
Disproportionative condensation ←
Modified Guerbet condensation
s. *9*, 275

Via intermediates *v.i.*

Carboxylic acid esters from carboxylic acids via mixed alkoxyformic acid anhydrides COOH → COOR
s. *9*, 276

Phosphonic and phosphinic esters from the acids ←

172.



o-Bromobenzenephosphonic acid and ca. 10% excess PCl_5 refluxed 30 min., $POCl_3$ and excess PCl_5 removed in vacuo, the residue dissolved in dry CCl_4. abs. ethanol added, and refluxed 1 hr. → diethyl o-bromobenzenephosphonate. Y: 75%. Also phosphinic acid esters s. L. D. Freedman et al., Am. Soc. *75*, 1379 (1953).

Nitrogen ↑ OC⇅N

Without additional reagents *w.a.r.*

Cleavage of nitramines ←
Steric hindrance s. *6*, 221

1-Methoxy-1-cyclohexen-3-ones from 1,3-cyclohexanediones ←
s. *8*, 89

Methylation of hydroxycoumarins ←
Coumarin-chromone tautomerism
Reaction-kinetic dependency
s. *7*, 250

4-Pyridones from 4-nitropyridines ←
s. *7*, 463

Carboxylic acid esters from carboxylic acids COOH → COOR
s. *8*, 232; *9*, 476

Dicarboxylic acid amide esters
from dicarboxylic acid monoamides

73. $H_2NCO[CF_2]_4COOH \rightarrow H_2NCO[CF_2]_4COOC_2H_5$

A soln. of crude perfluoroadipamic acid in ether added to ethereal diazoethane, and allowed to stand 20 min. at room temp. → ethyl perfluoroadipamate. Y: 86.5%. W. H. Rauscher and H. Tucker, Am. Soc. *76*, 3599 (1954).

Carboxylic acid esters from iminoesters C(:NH)OR → COOR
s. *8*, 251

Aminocarboxylic acid esters from ←
quaternary cyanoammonium salts via betaines
s. *6*, 222

Carboxylic acid alkoxymethylamides ←
from acylaminomethylpyridinium salts
s. *8*, 437

Phenols from diazonium salts ←
s. *6*, 223

Trialkyl- from dialkyl-oxonium salts ←
s. *9*, 990; s. a. B. *86*, 1322 (1953)

Benzo-1,3-dioxoles from diazo compounds and o-quinones ○
s. *8*, 233

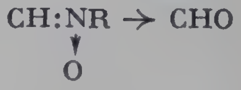
Irradiation ←

Carboxylic acids and esters from α-diazoketones ←
Carboxylic acids s. *8*, 919

174. $CCl_3CCl_2COCHN_2 \rightarrow [CCl_3CCl_2CH_2COOCH_3] \rightarrow CCl_3CCl{=}CHCOOCH_3$
with simultaneous dehydrohalogenation. Alkali-sensitive or slow-reacting α-diazoketones can be successfully converted into carboxylic acids or esters by irradiation.—E: Diazomethyl pentachloroethyl ketone in abs. methanol treated with filtered UV-Light for 8 hrs. → methyl β,γ,γ,γ-tetrachlorocrotonate. Y: 71%.—For the preparation of acids, it may be preferable to decompose the α-diazoketone in methanol and to hydrolyze the resulting ester instead of preparing the acids directly in dioxane-water (cf. Synth. Meth. *8*, 919). A. Roedig and H. Lunk, B. *87*, 971 (1954).

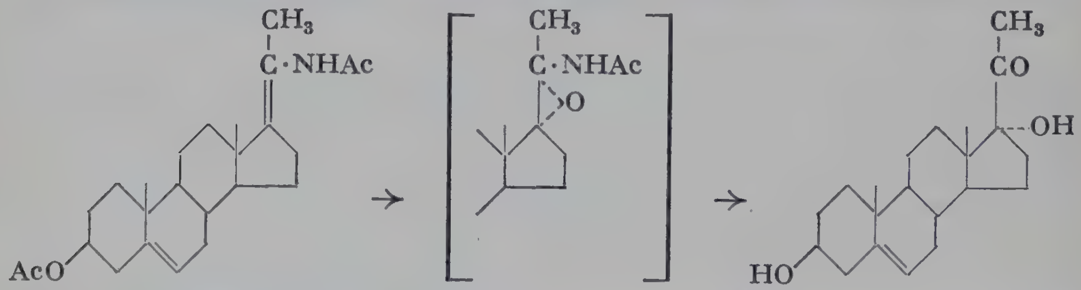
Sodium hydroxide *NaOH*

Aldehydes from nitrones
s. *9*, 553


$\underset{\overset{\downarrow}{O}}{CH{:}NR} \rightarrow CHO$

α-Hydroxyketones from enacetamines via 1,2-oxido-acetamines ←

175.



A soln. of perbenzoic acid in benzene-toluene added with stirring at 0° during 1 hr. to a soln. of 20-acetamino-3β-acetoxy-5,17(20)-pregnadiene (prepn. s. 298) in benzene-toluene, stirring continued for 20 min. until the perbenzoic acid has been consumed, the resulting crude 20-acetamino-3β-acetoxy-17,20-oxido-5-pregnene dissolved in cold methanol, 0.3 *N* NaOH added, and refluxed 1 hr. under N_2 → 17α-hydroxy-5-pregnen-3β-ol-20-one. Y: 64%. F. e. s. H. Ruschig et al., B. *88*, 883 (1955).

2-Imidazolidones from 2-nitraminoimidazolines ←
s. *8*, 234

Carboxylic acids from nitriles CN → COOH
s. *7*, 251

Degradation of peptides from the carboxyl end with carbodiimides via acylureas ←
s. *9*, 277

Phenoxazines ○
s. *9*, 509

Carboxylic acids from barbituric acids ⊂
s. *6*, 290

α-Aminocarboxylic acids from hydantoins
s. *6*, 761/2

Pyrrolo(2′,3′:3,4)isocoumarin ring opening
s. *9*, 740

Pyrimido[4,5-b]pyrazine ring opening
s. *9*, 278

Sodium hydroxide/pyridine $NaOH/C_5H_5N$

Carboxylic acids from nitriles CN → COOH
s. *9*, 279

Sodium hydroxide/hydrazine s. Hydrazine/sodium hydroxide $NaOH/H_2N{\cdot}NH_2$

Potassium hydroxide *KOH*

Ethers from quaternary ammonium salts ROR
s. *9*, 280

Oxo compounds from azomethines C:NR → CO
s. *9*, 857

Carboxylic acids from nitriles CN → COOH
s. *7*, 252; *9*, 769, 866

from cyanoketones s. *8*, 103	**from cyanocarboxylic acid esters** s. *6*, 700

Carboxythioethers from halogenonitriles
s. *9*, 691

α-Dicarboxylic acids from α-cyanocarboxylic acid esters
s. *7*, 253

Hydantoin ring opening
s. *8*, 30

Potassium hydroxide/alcohol

Replacement of mobile nitro groups by alkoxyl NO_2 → OR
s. *6*, 224

Carboxylic acids from nitriles CN → COOH
in n-propanol s. *1*, 189; in methanol s. G. W. Gray and B. Jones, Soc. *1954*, 678

Sodium/alcohol *NaOR*

Partial replacement of nitro groups by alkoxyl NO_2 → OR
s. *8*, 235

Ethers from quaternary ammonium salts ROR
s. *9*, 280; s. a. R. F. Long and A. L. Morrison, Soc. *1954*, 3854

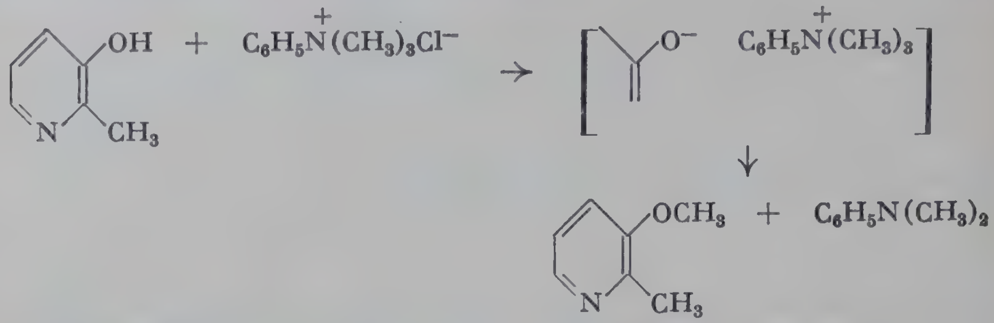
Rearrangement of isoxazolidones ←
s. *9*, 281

Enolethers from nitrocyclopropanes C
s. *6*, 225; *9*, 282

Sodium methoxide *$NaOCH_3$*

Selective O-methylation of phenolic bases $OH \rightarrow OR$

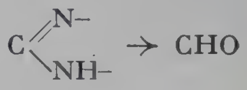
176.



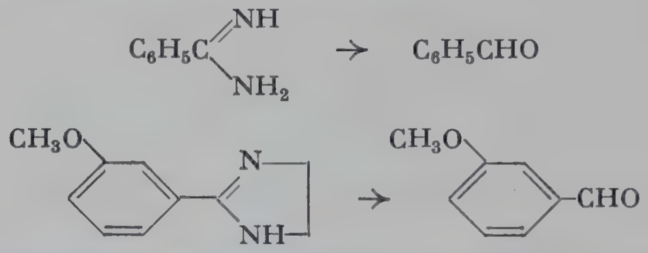
A soln. of 2-methyl-3-pyridol, Na-methoxide, and phenyltrimethylammonium chloride in dimethylformamide refluxed 2.5 hrs., and the product separated via its insoluble Cd-complex from the resulting dimethylaniline → 2-methyl-3-methoxypyridine. Y: 75%. B. R. Baker and F. J. McEvoy, J. Org. Chem. *20*, 136 (1955); f. e. s. *20*, 118.

Sodium/liq. ammonia/ethanol *$Na/NH_3/C_2H_5OH$*

Aldehydes from amidines and imidazolines



177.



Benzamidine allowed to react with Na and ethanol in liq. NH_3 → benzaldehyde. Y: ca. 100% as the 2,4-dinitrophenylhydrazone.—Similarly: 2-m-Methoxyphenylimidazoline → m-methoxybenzaldehyde. Y: 94% F. e. s. A. J. Birch, J. Cymerman-Craig, and M. Slaytor, Chem. and Ind. *1954*, 1559.

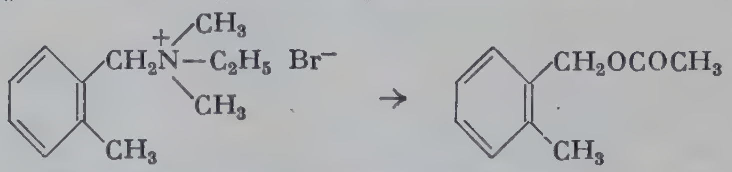
Sodium acetate *CH_3COONa*

Ketones from enamines ←
s. *8*, 428

Carboxylic acids from prim. nitro compounds $CH_2NO_2 \rightarrow COOH$
s. *6*, 227

Acoxy compounds from quaternary ammonium salts $\overset{+}{N}R_3 \rightarrow OAc$

178.



A soln. of (2-methylbenzyl)dimethylethylammonium bromide and freshly fused Na-acetate in glacial acetic acid refluxed 24 hrs. → 2-

methylbenzyl acetate. Y: 91%. F. e. s. W. R. Brasen and C. R. Hauser, J. Org. Chem. *18*, 806 (1953); Org. Synth. *34*, 58 (1954).

Sodium nitrite *$NaNO_2$*

Cleavage of nucleosides $NH_2 \rightarrow OH$
with subsequent replacement of amino groups by hydroxyl
s. *6*, 44

Replacement of imino groups by oxygen $C{:}NH \rightarrow CO$
s. *9*, 283

Oxo compounds from oximes $C{:}NOH \rightarrow CO$
s. *7*, 254

Ketones from α-aminoalcohols with rearrangement ←
s. *7*, 255

Pyrrole ring opening ⊂
s. *9*, 284

Sodium nitrite/sodium hydroxide *$NaNO_2/NaOH$*

Alcohols from amines $NH_2 \rightarrow OH$
s. *8*, 236

Sodium nitrite/trifluoroacetic acid *$NaNO_2/CF_3COOH$*

Replacement of amino groups by hydroxyl $NH_2 \rightarrow OH$
Diazonium perhalogenocarboxylates
s. *9*, 285

Sodium nitrite/phosphoric acid *$NaNO_2/H_3PO_4$*

Phenols
s. *9*, 286

Ammonia *NH_3*

Carboxylic acids from barbituric acids ⊂
s. *6*, 225

Benzylamine *$C_6H_5CH_2NH_2$*

Cyclic ureas from cyclic nitroguanidines ←
s. *6*, 229

Cuprous oxide *Cu_2O*

Quinones from nitrosophenols ←
s. *8*, 237

Cupric oxide *CuO*

α-Alkoxyketones from α-diazoketones $COCHN_2 \rightarrow COCH_2OR$
s. *8*, 238

α-Alkoxyketones and carboxylic acid esters from α-diazoketones $COCHN_2 \begin{matrix} \nearrow COCH_2OR \\ \searrow CH_2COOR \end{matrix}$
s. *7*, 256

Silver oxide *Ag_2O*

Malonic acid esters from carboxylic acid bromides via diazo compounds ←
s. *6*, 795

Cupric carbonate *$CuCO_3$*

Cleavage of ketone 2,4-dinitrophenylhydrazones C:NNHR → CO

179. Ketones are produced in high yield by heating the 2,4-dinitro-(or 4-nitro-)phenylhydrazone on a steam bath with 80% or stronger formic acid and Cu-carbonate until the color disappears. R. Robinson, Nature *173*, 541 (1954).

Silver benzoate/triethylamine *$C_6H_5COOAg/(C_2H_5)_3N$*

Carboxylic acid esters from α-diazoketones $COCHN_2 \rightarrow CH_2COOR$
Improved Wolff rearrangement
in homogeneous medium

s. *7*, 257; unsatd. esters s. J. H. Wotiz and S. N. Buco, J. Org. Chem. *20*, 210 (1955); tert-butyl esters s. A. C. Cope and R. D. Smith, Am. Soc. *77*, 4596 (1955)

Cupric chloride *$CuCl_2$*

α-Acoxyketones from α-diazoketones $COCHN_2 \rightarrow COCH_2OAc$
α-Diazoketones as reagents for the
identification of carboxylic acids

s. *9*, 287

Silver nitrite/hydrochloric acid *$AgNO_2/HCl$*

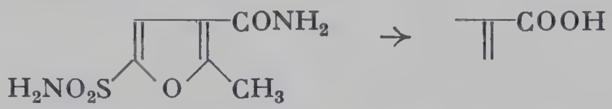
Aldehydes from hydrazones CH:NNHR → CHO

s. *8*, 145

Barium hydroxide *$Ba(OH)_2$*

Selective hydrolysis of carboxylic acid amides $CONH_2 \rightarrow COOH$
Sulfonylaminocarboxylic acids

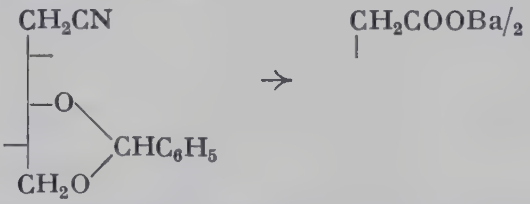
180.



2-Methyl-5-sulfonamido-3-furamide refluxed with aq. $Ba(OH)_2$ until no more NH_3 is evolved, then treated with CO_2 to remove Ba^{++} → 2-methyl-5-sulfonamido-3-furoic acid. Y: 70%. F. e. s. J. F. Scully and E. V. Brown, J. Org. Chem. *19*, 894 (1954).

Carboxylic acids from nitriles CN → COOH

181.



4,6-Benzylidene-2-deoxy-L-galactonitrile (prepn. s. 583) added to a soln. of $Ba(OH)_2$ in methanol-water, and heated 4-5 hrs. at 70° → Ba-4,6-benzylidene-2-deoxy-L-galactonate. Y: 91%. R. Grewe and H. Pachaly, B. *87*, 46 (1954).

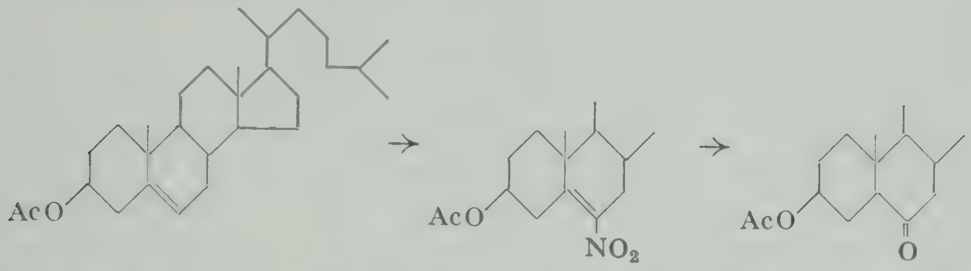
Labeled compounds
s. *6*, 230

α-Aminocarboxylic acids via hydantoins C
s. *9*, 832; cf. G. A. Stein, H. A. Bronner, and K. Pfister, 3rd, Am. Soc. *77*, 700 (1955)

Zinc/acetic acid *Zn/CH_3COOH*

Ketones from ethylene derivatives
via α-nitroethylene derivatives ←

182.



Steroids. Fuming HNO_3 added dropwise with stirring during 30 min. at 5-10° to a soln. of cholesteryl acetate in abs. ether, and stirring continued 1 hr. in the ice bath → 6-nitrocholesteryl acetate (Y: 72-79%) dissolved in glacial acetic acid, water added, then Zn-dust added in small portions during 4 hrs., refluxed after the initial exothermic reaction has subsided → cholestane-3β-ol-6-one acetate (Y: 73%). F. e. s. C. E. Anagnostopoulos and L. F. Fieser, Am. Soc. *76*, 532 (1954); R. M. Dodson and B. Riegel, J. Org. Chem. *13*, 424 (1948); cf. J. H. Pierce et al., Soc. *1955*, 694.

Zinc amalgam *Zn,Hg*

α-Hydroxycarboxylic acids from azlactones
Reductive oxazolone ring opening
s. *9*, 288

Zinc chloride *$ZnCl_2$*

Phenolethers and phenols from amines ←
via diazonium chloride-zinc chloride complex
s. *9*, 289

Lithium aluminum hydride *$LiAlH_4$*

Aldehydes from nitriles – Friedman reduction CN → CHO
s. *7*, 258

Boron fluoride *BF_3*

α-Alkoxyketones from α-diazoketones $COCHN_2 \rightarrow COCH_2OR$
s. *7*, 259

Clay or methyl alcohol ←

Ketoenolethers from β-diketones C:C(OR)
s. *7*, 260

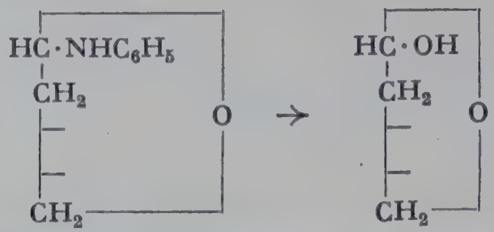
Formaldehyde/hydrochloric acid *CH_2O/HCl*

Ketones from oximes C:NOH → CO
s. *7*, 261

Benzaldehyde/benzoic acid C_6H_5CHO/C_6H_5COOH

Hydrolysis of glycosamines $N\langle \rightarrow OH$

183.



A mixture of 2-deoxy-D-ribose anilide, benzaldehyde, a little benzoic acid, and water shaken 22 hrs. at room temp. → 2-deoxy-D-ribose. Y: 94%. J. C. Sowden, Am. Soc. *76*, 3541 (1954).

Pyruvic acid $CH_3COCOOH$

Cleavage of hydrazones $C{:}NNHR \rightarrow CO$
s. *6*, 290, 891

Cleavage of semicarbazones $C{:}NNHCONH_2 \rightarrow CO$
s. *6*, 891

Hexamethylenetetramine $C_6H_{12}N_4$

Aldehydes from amines $CH_2N\langle \rightarrow CHO$
s. *8*, 239

from tert. amines
s. *9*, 290; s. a. M. M. and B. L. Robison, Am. Soc. *77*, 457 (1955)

Amino acid oxidase/catalase/oxygen ←

α-Ketocarboxylic acids from α-aminocarboxylic acids $CH(NH_2)COOH \rightarrow COCOOH$
s. *9*, 291

Streptococcus faecalis ←

Ureas from guanidines $NHC({:}NH)NH_2 \rightarrow NHC({:}O)NH_2$
s. *9*, 292

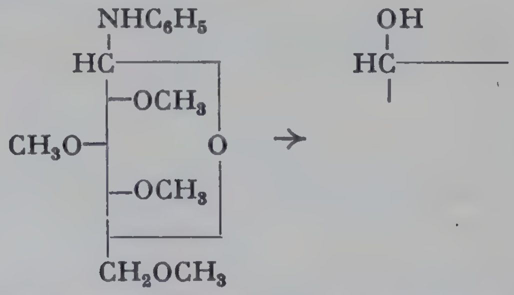
Acetic anhydride $(CH_3CO)_2O$

Acoxy compounds from tert. amines $NR_2 \rightarrow OAc$
s. *6*, 731

Cation exchange resin ←

Hydrolysis of carbohydrate anilides and sugar acid phenylhydrazides ←

184.



A suspension of 2,3,4,6-tetra-O-methyl-D-glucose anilide and Amberlite IR 120 in water containing 10-20% ethanol refluxed 20-60 min. until dissolved → 2,3,4,6-tetra-O-methyl-D-glucose. Y: 93%.—The base liberated in the reaction is absorbed by the resin thus facilitating the isolation of the product. F. e., also cleavage of sugar acid phenylhydrazides, s. G. W. Huffman and F. Smith, Am. Soc. *77*, 3141 (1955).

Acetic acid *CH_3COOH*

Hydrolysis of glycosamines N< → OH
s. *7*, 417

α-Diketones from α-hydroxyhydrazones CH(OH)C:NNHR → COCO
s. *8*, 240

Trifluoroacetic acid/sodium nitrite *$CF_3COOH/NaNO_2$*
s. Sodium nitrite/trifluoroacetic acid

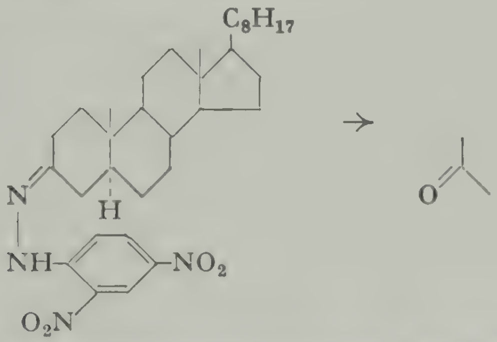
Oxalic acid *$(COOH)_2$*

Cleavage of semicarbazones $C{:}NNHCONH_2 \rightarrow CO$
s. *1*, 195; s. a. A. C. Cope, D. C. McLean, and N. A. Nelson, Am. Soc. *77*, 1628 (1955)

Stannous chloride/hydrochloric acid *$SnCl_2/HCl$*

Cleavage of 2,4-dinitrophenylhydrazones C:NNHR → CO

185.



Cholestan-3-one 2,4-dinitrophenylhydrazone dissolved in acetone containing concd. HCl, refluxed 45 min. or allowed to stand at room temp. for 24 hrs., slightly cooled, treated with a soln. of $SnCl_2$ in concd. HCl, water added, refluxed under N_2 for 45 min. or allowed to stand 24 hrs. at room temp. → cholestan-3-one. Y: 98%. F. e. s. J. Demaecker and R. H. Martin, Nature *173*, 266 (1954); s. a. J. J. Beereboom and C. Djerassi, J. Org. Chem. *19*, 1196 (1954).

Thiosemicarbazones from nitriles via aldehydes CN → CHO
Stephen reduction
s. *7*, 262

Hydrazine/sodium hydroxide *$H_2N{\cdot}NH_2/NaOH$*

Dicarboxylic acids ←
from cyanoketocarboxylic acid esters
s. *10*, 141

Hydroxylamine *H_2NOH*

Ring opening of isocyclics C
s. *8*, 241

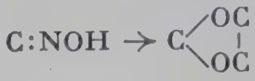
Dinitrogen trioxide N_2O_3

Carboxylic acids from carboxylic acid amides $CONH_2 \rightarrow COOH$

s. *5*, 185; with liq. N_2O_3 s. R. Grewe and G. Rockstroh, B. *86*, 536 (1953)

Butyl nitrite/sulfuric acid C_4H_9ONO/H_2SO_4

Acetals from oximes
s. *7*, 610



$C{:}NOH \rightarrow C\begin{cases} OC \\ | \\ OC \end{cases}$

Nitrosyl chloride $NOCl$

Carboxylic acids from carboxylic acid amides $CONH_2 \rightarrow COOH$
s. *7*, 263

Nitric acid HNO_3

Quinones ←

from acylaminophenols
s. *7*, 264

Nitric acid/ether $HNO_3/(C_2H_5)_2O$

from aminophenols
s. *9*, 293

Phosphoric acid H_3PO_4

Replacement of amino groups by hydroxyl $NH_2 \rightarrow OH$
s. *6*, 231

Phosphoric acid/sodium nitrite $H_3PO_4/NaNO_2$
s. Sodium nitrite/phosphoric acid

Ozone O_3

Cleavage of hydrazones $C{:}NNHR \rightarrow CO$
s. *8*, 242

Sulfur dioxide SO_2

Replacement of amino groups by hydroxyl $NH_2 \rightarrow OH$
Modified Bucherer reaction

s. *4*, 224; critical temp. s. H. Rapoport, R. H. Allen, and M. E. Cisney, Am. Soc. *77*, 670 (1955)

Nitrosyl sulfate $ONOSO_3H$

Subst. carboxylic acid amides ←
from hydrazones and semicarbazones by rearrangement
s. *9*, 294

Sulfuric acid H_2SO_4

Replacement of amino groups by hydroxyl $NH_2 \rightarrow OH$
s. *7*, 265

Enols from enamines $C{:}C{\cdot}N\langle \rightarrow C{:}C{\cdot}OH$
s. *7*, 266

Steam volatile phenols from diazonium salts $\overset{+}{N}_2 \rightarrow OH$
s. *7*, 267

o-Dihydroxy compounds from o-aminohydroxy compounds via diazo oxides $NH_2 \rightarrow OH$
s. *7*, 268

Acetates from nitrates – Simple acetolysis $ONO_2 \rightarrow OAc$
s. *7*, 269

Oxo compounds from imines C:NH → CO
s. *7*, 270

Ketones
s. *9*, 295

Ketones from oximes C:NOH → CO
s. *7*, 240

Nef reaction

Ketones from aci-nitro compounds $CH(NO_2) \rightarrow CO$
s. *8*, 243

Synthesis of carbohydrates via nitropolyalcohols
s. *8*, 244; cf. J. K. N. Jones, Soc. *1954*, 3643

Aldehydes from 1,1-dicarbalkoxyamines $CH(NHCOOR)_2 \rightarrow CHO$
s. *8*, 319

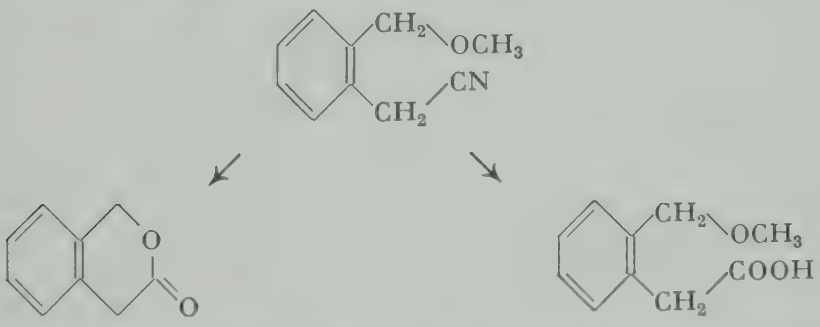
Oxo compounds from acylhydrazones C:NNHAc → CO
s. *9*, 431

α-Hydroxyketones from α-diazoketones $COCHN_2 \rightarrow COCH_2OH$
s. *9*, 296

Carboxylic acids from nitriles CN → COOH
s. *8*, 832

Lactones from alkoxynitriles ○
3,6-Dihydro-4,5-benzo-2-pyrones

86.



A mixture of o-methoxymethylbenzyl cyanide and aq. H_2SO_4 refluxed 6 hrs. with stirring → 3,6-dihydro-4,5-benzo-2-pyrone. Y: 87%.—Hydrolysis in aq.-alc. NaOH gives o-methoxymethylphenylacetic acid. F. G. Mann and F. H. C. Stewart, Soc. *1954*, 2819.

Sulfuric acid/acetic acid *H_2SO_4/CH_3COOH*

Carboxylic acids from nitriles CN → COOH
s. *9*, 297

Chromic acid CrO_3

Quinones from nitrosophenols via aminophenols ←
s. *8*, 245

Carboxylic acids from aldoximes ←
s. *6*, 233

Hydrochloride ←

Iminoesters from amidines and orthoformic acid esters ←
s. *6*, 234

Pyridine hydrochloride C_5H_5N,HCl

3-Arylcoumarins from aldehydes via α,β-ethylenenitriles ○
Lactones from alkoxynitriles
s. *7*, 271

Hydrochloric acid HCl

Ketones from enamines $CH{:}C\cdot N< \rightarrow CH_2CO$
s. *7*, 217

Replacement of amino groups by oxygen ←
s. *9*, 298

Oxo compounds from imines $C{:}NH \rightarrow CO$
s. *6*, 483; *10*, 257

Isatins from 2-iminoisatins
s. *6*, 871

1,3(2H)-Benzoxathiol-2-ones from 2-imino-1,3(2H)-benzoxathioles
s. *7*, 614

Oxo compounds from azomethines $C{:}NR \rightarrow CO$
s. *6*, 235; *9*, 730

Aldehydes	**Ketones**
s. *8*, 835	s. *7*, 854

Naphtho[2,3]-1,3-dithioles ←
Oxo compounds from immonium salts
s. *8*, 246

Ketones from oximes $C{:}NOH \rightarrow CO$
Optically active compounds
s. *7*, 272

Coumarandiones from 2-oximinocoumaran-3-ones
s. *8*, 214

Cyclohexenones via nitrocyclohexenes ←
Nef reaction with preceding diene synthesis
s. *9*, 299

Hydrolysis of 1-alkoxy-1-acylamino compounds ←
s. *8*, 247

Aldehydes from amidines via 1,1-diamines ←
N-Carbethoxyamidines
Prepn. of aluminum amalgam
s. *6*, 237

Aldehydes from hydrazones CH:NNHR → CHO
Cleavage of Girard derivatives
s. *6*, 236; s. a. D. A. Forss and E. A. Dunstone, Nature *173*, 401 (1954)

Carboxylic acids from nitriles CN → COOH
s. *6*, 238; *7*, 273; *8*, 170; *10*, 537

Carboxylactones from cyanolactones
s. *9*, 826

Carboxylic acid esters from nitriles CN → COOR
s. *10*, 164, 675

α-Acoxycarboxylic acid esters
s. *6*, 239

Cyanocarboxylic acid esters from dinitriles
s. *7*, 274

Dicarboxylic acids from dicyanocarboxylic acid esters ←
s. *6*, 705

Carboxylic acids from acylureas $CONHCONH_2$ → COOH
s. *8*, 248

Lactones from nitronitriles ○
s. *8*, 344

Hydantoins from α-ureidonitriles
s. *9*, 245

1-Subst. hydantoins
s. *9*, 300

Carboxylic acid esters from 1,3,5-triazines C
s. *7*, 275

Hydrobromic acid *HBr*

Lactones from alkoxynitriles ○
s. *6*, 240

Coumarin ring
9,10-Dihydro-10-keto-2-aza-9-oxaphenanthrenes
s. *8*, 249

Aminodicarboxylic acids from cyanolactams C
s. *10*, 529

Manganese dioxide MnO_2

Phosphorylation with subsequent
formation of aldehydes from amines CH_2NH_2 → CHO
s. *8*, 250

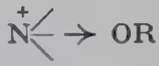
Iron/ferric chloride *Fe/FeCl₃*

Ketones from 1,1-nitroethylene derivatives $CH{:}C(NO_2) \rightarrow CH_2CO$
s. *6*, 241; s. a. T. C. Myers et al., Am. Soc. *77*, 5655 (1955); R. V. Heinzelman, Org. Synth. *35*, 74 (1955)

Ferric chloride *FeCl₃*

Quinones from nitrosophenols via aminophenols ←
s. *7*, 276

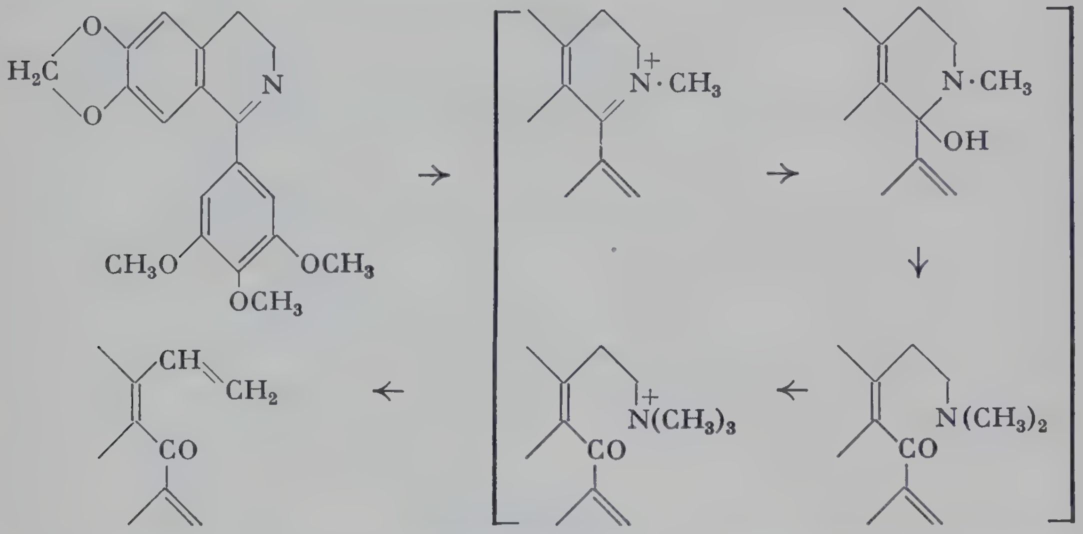
Via intermediates *v.i.*

Ethers from quaternary ammonium salts

s. *7*, 811

Carboxylic acid esters from nitriles via iminoesters CN → COOR
s. *8*, 251

Ethyleneketones from N-heterocyclics via pseudobases and tert-aminoketones

187.



A mixture of 1-(3′,4′,5′-trimethoxyphenyl)-6,7-methylenedioxy-3,4-dihydroisoquinoline, dimethyl sulfate, and aq. NaOH heated 6 hrs. → 2-(3′,4′,5′-trimethoxybenzoyl)-4,5-methylenedioxystyrene. Y: ca. 100%. Also isolation of the intermediates s. W. J. Gensler and C. M. Samour, Am. Soc. *74*, 2959 (1952).

Halogen ↑ OC ⇅ Hal

Without additional reagents *w.a.r.*

Selective replacement of chlorine by hydrogen with subsequent replacement of chlorine by hydroxyl Cl → OH
s. *8*, 252

Bromohydrins from 1,2-dibromides CBrCBr → C(OH)CBr
s. *9*, 307

Partial replacement of bromine by hydroxyl and alkoxyl Br → OH, → OR
s. *7*, 277

Aminoethers from aminoalcohols Hal → OR
s. *9*, 301

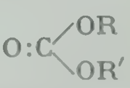
Glycosides from benzoylated halogenosugars
Debenzoylation
s. *8*, 253

1,2-Diacetals from 1,2-dialkoxy-1,2-dihalides ←
s. *7*, 218

Carboxylic acids-d from carboxylic acid chlorides COCl → COOD
s. *8*, 134a

Reactions with fluoro compounds ←
Carboxylic acid amides from 1,1,1-dihalogenamines
s. *9*, 302

Mixed carbonic acid esters



$O{:}C\begin{smallmatrix}OR\\OR'\end{smallmatrix}$

188. p–$O_2NC_6H_4CH_2OCOCl$ + $HOCH_3$ → p–$O_2NC_6H_4CH_2OCOOCH_3$

p-Nitrobenzyl chloroformate dissolved in methanol and allowed to stand overnight at room temp. → methyl p-nitrobenzyl carbonate. Y: 91%. Also O,N-derivatives s. D. T. Gish and F. H. Carpenter, Am. Soc. *75*, 950 (1953); f. e. s. Am. Soc. *74*, 3818 (1952).

Benzo-1,3-dioxoles ○
s. *8*, 254

2′,4-Dioxopyrano(3′,4′:5,6)-1,3-dioxins from malonyl chloride and ketones
s. *10*, 612

1,3,4-Dioxazol-2-ones from hydroxamic acids and phosgene
s. *8*, 255

Sodium *Na*

1,2-Diglycerides
Blocking of hydroxyl groups by formation of benzyl ethers Hal → OR
s. *9*, 303

O-Acylation OH → OAc
s. *9*, 304

Potassium *K*

α-Alkoxycarboxylic acid esters from α-bromocarboxylic acid chlorides CBr·COCl → C(OR)·COOR
s. *6*, 242

Carbalkoxyenolethers from β-ketocarboxylic acid esters $COCH_2COOR \rightarrow C(OR'){:}CHCOOR$
s. *6*, 243

Sodium hydroxide *NaOH*

Replacement of chlorine by hydroxyl Cl → OH
s. *9*, 305

via sulfonic acids
s. *9*, 306

Ethers – Carbohydrate derivatives ROR
s. *7*, 307

Replacement of halogen by alkoxyl Hal → OR
1,3,5-Triazine derivatives
s. *8*, 256

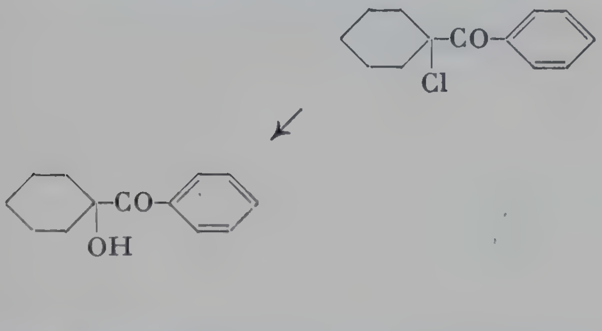
Hydroxyethers from halogenhydrins
s. *8*, 257

Halogenethers from dihalides
s. *9*, 312

1,3-Dialdehydes from β-halogeno-α,β-ethylenealdehydes ←
s. *8*, 258

α-Hydroxyketones and carboxylic acids from α-halogenoketones ←

189.



α-Chlorocyclohexyl phenyl ketone added to a suspension of NaOH in ether, and stirred 48 hrs. → α-hydroxycyclohexyl phenyl ketone. Y: 83%.

A mixture of α-chlorocyclohexyl phenyl ketone, NaOH, and xylene refluxed 30 hrs. with stirring → 1-phenylcyclohexanecarboxylic acid (Y: 53%) and α-hydroxycyclohexyl phenyl ketone (Y: 25%).

Also with the bromoketone s. C. L. Stevens and E. Farkas, Am. Soc. *74*, 5352 (1952).

Carboxylic acids from 1,1,1-trihalides $CHal_3 \rightarrow COOH$

from 1,1,1-trifluorides
s. *8*, 259

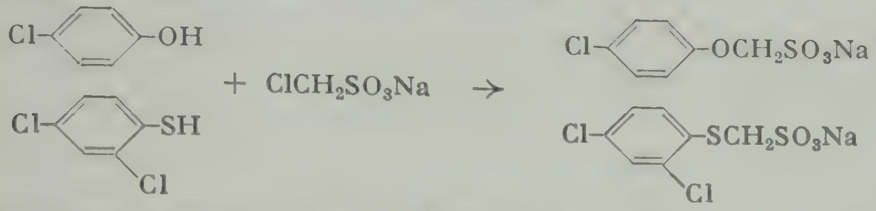
with simultaneous dehydration
s. *7*, 868

2-Pyridones from 2-halogenopyridinium salts ←
s. *8*, 287

Monoperoxycarbonic acid esters from hydroperoxides ←
s. *7*, 278

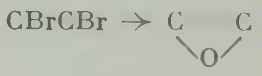
Aryloxy- and arylthio-methanesulfonates ←

190.



The calculated quantity of aq. 50%-NaOH added to a mixture of equimolar amounts of Na-chloromethanesulfonate monohydrate and 4-chlorophenol, heated slowly to 200°, maintained at that temp, until no more water distills off, and heating continued 4 hrs. at 200-240° → Na-p-chlorophenoxymethanesulfonate. Y: 83%.—Similarly with 2.4-dichlorothiophenol → Na-2.4-dichlorophenylthiomethanesulfonate. Y: 98%. F. e. s. H. J. Barber et al., J. Appl. Chem. *3*, 253 (1953).

Oxido compounds and bromohydrins from 1,2-dibromides
s. *9*, 307



Carbonic acid esters ←
s. *9*, 308

Sodium hydroxide/alcohol

Acetals from α,β-ethylenehalides $CH(OR)_2$
s. *7*, 279

Potassium hydroxide *KOH*

Replacement of halogen by hydroxyl Hal → OH
N-Oxides as intermediates
s. *8*, 260

Phenol ethers from halides Hal → OR
s. *6*, 244

α-Halogen-α,β-ethylenecarboxylic acids from α,α,α′-trihalogenoketones ←
s. *7*, 280

Peroxycarboxylic acid esters from hydroperoxides COO_2R
s. *8*, 261

p-Dioxanes by dimerization

s. *9*, 309

Carboxylic acids from cyclic α-halogenoketones ←
Ring contraction
Benzene ring from tropone ring
s. *9*, 310

Benzofurans via 3-chlorocoumarins ←
Perkin transformation
s. *6*, 784

Potassium hydroxide/alcohol
Ethers from halides Hal → OR
s. *9*, 311

Halogenethers from dihalides
s. *9*, 312

Sodium/alcohol *NaOR*
Ethers from halides Hal → OR
s. *6*, 245/6

Basic ethers – Williamson reaction
s. *7*, 281

Alkoxyacetals from halogenacetals

191. $n\text{-}C_3H_7OH + BrCH_2CH(OC_3H_7\text{-}n)_2 \rightarrow n\text{-}C_3H_7OCH_2CH(OC_3H_7\text{-}n)_2$

Na dissolved in n-propanol under H_2, bromoacetaldehyde dipropylacetal added, heated 6 hrs. at 160° and 230 atm. H_2, then allowed to cool over a period of 16 hrs. → propoxyacetaldehyde dipropylacetal. Y: 95%. F. e. s. H. Baganz, K.-H. Dossow, and W. Hohmann, B. *86*, 148 (1953).

Replacement of chlorine by alkoxyl Cl → OR
s. *9*, 313

Selective replacement
s. *6*, 247

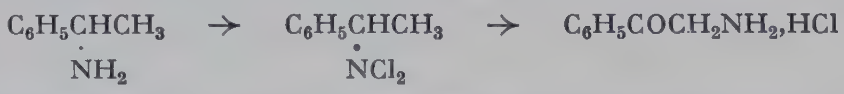
Simultaneous O- and C-methylation ←
s. *9*, 882

3-Alkoxyethylene derivatives from 1,2-dihalides ←
s. *8*, 262

Hydroxyethers from halogenhydrins and oxido compounds ←
s. *8*, 263

α-Aminoketones from amines ←
via N,N-dichloroamines with rearrangement

192.



$$C_6H_5\underset{NH_2}{C}HCH_3 \rightarrow C_6H_5\underset{NCl_2}{C}HCH_3 \rightarrow C_6H_5COCH_2NH_2{,}HCl$$

α-Phenylethylamine added slowly with stirring below 10° to aq. K-hypochlorite soln., then acetic acid added dropwise below 10°, and stirring continued for 2 hrs. at the same temp. → N,N-dichloro-α-phenylethylamine (Y: 82-92%) dissolved in abs. methanol, added dropwise with vigorous stirring to a hot soln. of Na in abs. methanol at such a rate as to maintain gentle reflux, heated 15 min. on a steam bath with continued stirring, and the product isolated as the hydrochloride → phenacylamine hydrochloride (Y: 52%).—The simple operation and easy isolation of the products may recommend this method where the amine is readily available. F. e. s. H. E. Baumgarten and F. A. Bower, Am. Soc. *76*, 4561 (1954).

Carboxylic acid esters from α-halogenoketones ←
s. *9*, 314

α,β-Ethylenecarboxylic acid esters from α,α′-dihalogenoketones ←
Modified Favorskii rearrangement
s. *7*, 283

α-Alkoxycarboxylic acids from α-halogenocarboxylic acid esters ←
s. *8*, 264

δ-Ketocarboxylic acid esters $COOH \rightarrow COOR$
from δ-ketocarboxylic acids
s. *8*, 265

Orthocarboxylic acid esters from 1,1,1-trihalides $CHal_3 \rightarrow C(OR)_3$
s. *7*, 282

Orthocarbonic acid esters $C(OR)_4$
s. *8*, 266

Sodium methoxide $NaOCH_3$

α,β-Ethylenecarboxylic acid esters ←
from methyl α,β-dibromoketones
s. *6*, 248

Sodium n-butoxide $NaOC_4H_9\text{-}n$

Alkoxycarboxylic acids via alkoxycarboxylic acid esters $Hal \rightarrow OR$
Selective hydrolysis
s. *8*, 267

Potassium/alcohol KOR

Arylethers from arylhalides
Steric hindrance s. *8*, 268

Aromatization of α-aminomethyleneketones ←
s. *9*, 315

Potassium/liq. ammonia K/NH_3

Ethers – Carbohydrate derivatives ROR
s. *8*, 269

Sodium peroxide Na_2O_2

Peroxydicarbonic acid esters from chloroformic acid esters ←
s. *7*, 284

Sodium carbonate Na_2CO_3

Partial and selective replacement of chlorine by hydroxyl $Cl \rightarrow OH$
s. *8*, 270; s. a. P. J. Ashworth, G. H. Mansfield, and M. C. Whiting, Org. Synth. *35*, 20 (1955)

α-Hydroxycarboxylic acids
from α-chlorocarboxylic acid chlorides

193. $(p\text{-}ClC_6H_4)_2CClCOCl \rightarrow (p\text{-}ClC_6H_4)_2C(OH)COOH$

Bis-(p-chlorophenyl)-α-chloroacetyl chloride added to aq. Na-carbonate, and refluxed 1 hr. → p,p′-dichlorobenzilic acid. Y: 73%. C. M. Welch and H. A. Smith, Am. Soc. *75*, 1412 (1953).

Sodium hydrogen carbonate *$NaHCO_3$*

Glycols from chlorohydrins C(OH)CCl → C(OH)C(OH)
s. *7*, 285

Basic ethers ROR
s. *7*, 281

Potassium carbonate *K_2CO_3*

Ethers
s. *8*, 271

Partial etherification
s. *7*, 286; s. a. V. K. Ahluwalia, S. K. Mukerjee, and T. R. Seshadri, Soc. *1954*, 3988

Carboxylic acids from cyclic α-halogenoketones ←
Ring contraction
s. *7*, 287

Potassium carbonate/sodium iodide *K_2CO_3/NaI*

Ethers ROR
s. *7*, 288

Potassium hydrogen carbonate *$KHCO_3$*

Replacement of halogen by acoxy groups Hal → OAc
s. *9*, 642

Acetates from bromides via iodides
s. *7*, 289

Sodium formate *HCOONa*

Replacement of halogen by hydroxyl Hal → OH
s. *6*, 249

Formoxy compounds from bromides Br → OCHO
s. *8*, 159

Potassium acetate *CH_3COOK*

Replacement of bromine by acetoxy groups Br → OAc
s. *7*, 290

in silanes, also cleavage
s. *9*, 316

α-Acoxy- from α-iodoketones CO·CI → COC(OAc)
s. *10*, 162

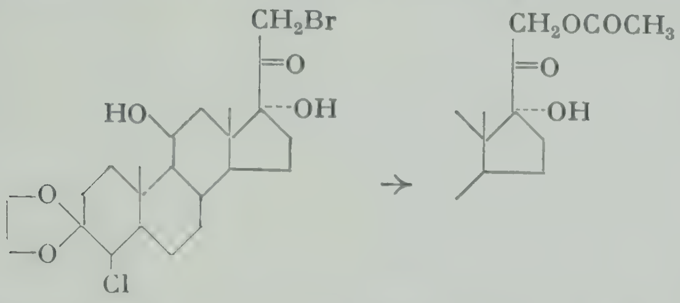
Glycol acetates from ethylene derivatives via bromohydrins ←
Polyalcohol derivatives
Steric effects
s. *8*, 272

α-Diketones from α-halogeno-α,β-ethyleneketones ←
s. *7*, 291

Potassium acetate/potassium iodide *CH_3COOK/KI*

Selective replacement of halogen by acetoxy groups Hal → OAc

194.



K-acetate, glacial acetic acid, and a little KI added to 4-chloro-21-bromo-11β,17α-dihydroxypregnane-3,20-dione 3-ethylene ketal in acetone, and refluxed 16 hrs. with stirring → 4-chloro-21-acetoxy-11β,17α-dihydroxypregnane-3,20-dione 3-ethyleneketal. Y: 96.6%. R. H. Levin et al., Am. Soc. *76*, 546 (1954).

Potassium oxalate *$(COOK)_2$*

Aldehydes from 1,1-dihalides $CHHal_2$ → CHO
s. *7*, 292

Sodium iodide *NaI*

Alkoxycarboxylic acids via alkoxycarboxylic acid esters Hal → OR
Selective hydrolysis
s. *8*, 273

Potassium iodide *KI*

Phthalimidomethylene ethers as used for the characterization of hydroxy compounds ←
s. *7*, 293

Sodium salt *Na^+*

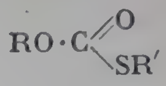
Arylethers ArOR
s. *9*, 953

Bis(aryloxy)methanes H_2CHal_2 → $H_2C(OAr)_2$
s. *8*, 274

Carboxylic acid anhydrides from carboxylic acid chlorides RCO·O·OCR′
s. *9*, 317

Unsym. acyl peroxides $RCO \cdot O_2 \cdot OCR'$
s. *7*, 294

Thiocarbonic acid esters
from thiocarbonic acid chlorides
s. *7*, 295



$RO\cdot C{\scriptstyle\genfrac{}{}{0pt}{}{/\!\!/O}{\backslash SR'}}$

Potassium salt K^+

Ethers from halides $Hal \rightarrow OR$
s. *7*, 296

Diethylamine $(C_2H_5)_2NH$

Phenolcarboxylic acid esters $COOH \rightarrow COOR$
from phenolcarboxylic acids
s. *7*, 297

Trialkylamine R_3N

Mixed alkoxyformic acid anhydrides $(RO)CO\cdot O\cdot OCR'$
s. *7*, 447

Triethylamine $(C_2H_5)_3N$

Acoxy compounds from halides $Hal \rightarrow OAc$
s. *7*, 298

Urethans from hydroxy compounds $OH \rightarrow OCON\langle$
s. *7*, 299

Dimethylaniline $C_6H_5N(CH_3)_2$

Hydroxyurethans from diols via hydroxychloroformates ←
s. *7*, 300

N-Ethylpiperidine ←

Mixed carboxylic acid anhydrides $RCO\cdot O\cdot OCR'$
from carboxylic acid chlorides
s. *7*, 436

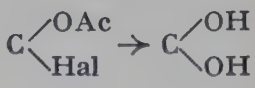
Mixed alkoxyformic acid anhydrides $(RO)CO\cdot O\cdot OCR'$
s. *8*, 528

Pyridine C_5H_5N

Ethers from halides $Hal \rightarrow OR$
s. *6*, 264; s. a. M. F. Grundon and H. J. H. Perry, Soc. *1954*, 3531

Selective etherification ROR
Triphenylmethyl ethers
s. *8*, 275

1,1-Dihydroxy compounds from 1,1-acoxyhalides
***α*-Ketoaldehyde hydrates**
s. *8*, 276



$C\genfrac{}{}{0pt}{}{/OAc}{\backslash Hal} \rightarrow C\genfrac{}{}{0pt}{}{/OH}{\backslash OH}$

Acylation of unstable alcohols $OH \rightarrow OAc$
s. *8*, 277

Glycerides
s. *9*, 318

  1,2-Diglycerides
  s. *9*, 303

1,2-Acoxyhalides from halogenhydrins
s. *10*, 196

Benzoylation of carbohydrates
s. *6*, 291, 296

O-Acylation of β-ketocarboxylic acid esters ←
s. *10*, 622

Selective acylation OH → OAc
s. *6*, 250; *9*, 319

Dehydration of alcohols via carbonic acid esters OH → OCOOR
s. *8*, 915

O-Carbethoxylation OH → $OCOOC_2H_5$
s. *9*, 320

Partial O-carbethoxylation
Protection of steroid 3-hydroxyl groups
s. *7*, 301

Orthocarboxylic acid esters from 1,1-dialkoxy-1-chlorides ←
s. *8*, 278

Sym. diperoxycarbonic acid esters from hydroperoxides ←
s. *7*, 302

Carboxylic acid anhydrides RCOCl + HOOCR → RCO·O·OCR
from carboxylic acid chlorides and carboxylic acids
s. *9*, 321

Alkoxylactones from ketocarboxylic acids ○
s. *7*, 303

Pyridine/silver nitrate s. Silver nitrate/pyridine $C_5H_5N/AgNO_3$

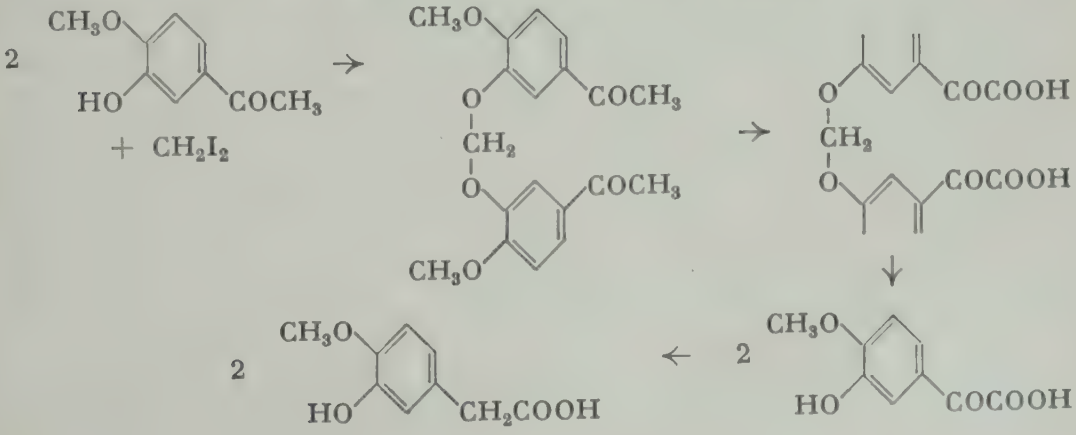
Copper *Cu*

Phenols from halides Hal → OH
with NaOH s. *6*, 251; with KOH s. D. E. Janssen, J. VanAllan, and C. V. Wilson, J. Org. Chem. *20*, 1326 (1955)

Diaryl ethers – Ullmann reaction ArOAr
s. *2*, 255; *4*, 240; s. a. H. Stetter and G. Duve, B. *87*, 1699 (1954)

Carboxylic acids from methyl ketones via α-ketocarboxylic acids ←
Protection of phenol groups by formation of formals

95.



A soln. of isoacetovanillone in abs. alcohol, methylene iodide, and Cu-bronze added to a soln. of Na in abs. alcohol, then refluxed 30 hrs. → formaldehyde-bis-isoacetovanillone acetal (Crude Y: 67%) suspended in aq. NaOH, and treated with 2% excess of a warm 5%-$KMnO_4$ soln. at 70-80° during 1.5 hrs. → formaldehyde-bis-isovanilloylformic acid acetal (Crude Y: 60%) refluxed 1.5 hrs. with 3 *N* HCl → isovanilloylformic acid (Y: 70%) dissolved in abs. alcohol, treated with hydrazine hydrate, then a soln. of Na in abs. alcohol added to the cold soln., heated slowly until alcohol, water, and excess hydrazine are distilled off, the bath temp. raised to 200°, and kept 15 min. at this temp. → homoisovanillic acid (Y: 84%). R. Schwarz and K. Capek, M. *83*, 883 (1952).

Tobin bronze

Methylenedioxyarenes ○
s. *8*, 279

Copper/calcium oxide *Cu/CaO*

Phenols from halides Hal → OH
s. *6*, 252

Cupric oxide *CuO*

Ethers from halides Hal → OR
s. *9*, 322

Silver oxide *Ag_2O*

O-Methylation
s. *2*, 256/7; tetrahydrofuran derivatives s. J. Kebrle and P. Karrer, Helv. *37*, 484 (1954)

Carboxylic acid anhydrides from carboxylic acid chlorides 2 COCl → CO·O·OC
s. *8*, 280

Silver oxide/iodine/calcium sulfate *$Ag_2O/I/CaSO_4$*

Di- from mono-saccharides ←
s. *8*, 281

Silver acetate *CH_3COOAg*

Replacement of halogen by acoxy groups Hal → OAc
s. *8*, 18

1,1-Diacoxy compounds from 1,1-acoxybromides CBr(OAc) → $C(OAc)_2$
Selective replacement of bromine by acoxy groups
s. *8*, 282

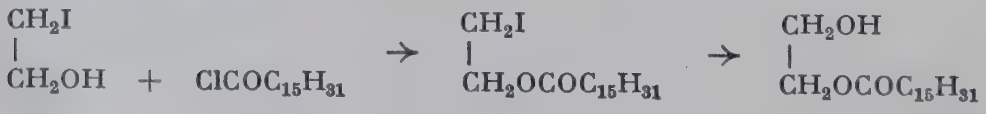
Cupric chloride *$CuCl_2$*

Ketones from 1,1-dichlorides CCl_2 → CO
s. *8*, 283

Silver nitrite *$AgNO_2$*

Glycol monoesters from halogenhydrins via 1,2-acoxyhalides Hal → OH

196.



$$\begin{array}{l}CH_2I\\ |\\ CH_2OH\end{array} + ClCOC_{15}H_{31} \rightarrow \begin{array}{l}CH_2I\\ |\\ CH_2OCOC_{15}H_{31}\end{array} \rightarrow \begin{array}{l}CH_2OH\\ |\\ CH_2OCOC_{15}H_{31}\end{array}$$

Palmitoyl chloride in dry benzene added sowly to ethylene iodohydrin in benzene containing pyridine, and allowed to stand overnight → 2-iodoethyl palmitate (Y: 93%) refluxed 45 min. with a soln. of $AgNO_2$ in ethanol-water → 2-hydroxyethyl palmitate (Y: 90-95%). F. e., also from bromohydrins, s. T. H. Bevan, T. Malkin, and D. B. Smith, Soc. *1955*, 1043.

Silver nitrate *$AgNO_3$*

Nitric acid esters from halides Hal → ONO_2

s. *9*, 323; s. a. Am. Soc. *77*, 4415 (1955); M. F. Hawthorne, Am. Soc. *77*, 5523 (1955)

Silver nitrate/pyridine *$AgNO_3/C_5H_5N$*

Ethylenealcohols from 1,2-dibromides ←

s. *6*, 253

Silver salt *Ag^+*

Replacement of halogen by acoxy groups Hal → OAc

Carbohydrates

s. *8*, 284

Carboxylic acid esters COOR

s. *9*, 324

Unsym. carboxylic acid anhydrides from carboxylic acid chlorides RCO·O·OCR′

197. $CF_3COOAg + ClCOC_6H_5 \rightarrow CF_3CO\cdot O\cdot COC_6H_5$

A soln. of benzoyl chloride in anhydrous ether added to a soln. of Ag-trifluoroacetate in the same solvent, AgCl removed after 30 min. by filtration, and the crude product flash distilled at 1.0 mm. and a bath temp. of 120° → benzoyl trifluoroacetate. Y: 80%.—Without *flash distillation*, acyl interchange takes place, and sym. anhydrides are isolated. F. e. s. A. F. Ferris and W. D. Emmons, Am. Soc. *75*, 232 (1953).

Phosphoric acid esters from halides Hal → $OPO(OR)_2$

98. $C_{16}H_{33}I + AgOPO(OC_6H_5)_2 \rightarrow C_{16}H_{33}OPO(OC_6H_5)_2$

Hexadecyl iodide in dry benzene refluxed 3 hrs. with vigorous stirring in the dark with silver diphenyl phosphate → diphenyl hexadecyl phosphate. Y: 92%.—The reaction fails or gives poor yields when carried out in the light. F. e. s. R. L. Baylis, T. H. Bevan, and T. Malkin, Chem. and Ind. *1955*, 67; carbohydrate derivatives s. T. Posternak, Helv. *36*, 1614 (1953).

Acylphosphoric acid esters ←

s. *7*, 304

Sulfonic acid esters ←

s. *9*, 325

Calcium carbonate *$CaCO_3$*

Ethers from halides Hal → OR

s. *8*, 285

Bromohydrins from 1,2-dibromides $CBrCBr \rightarrow C(OH)CBr$
s. *6*, 254

Aldehydes from 1,1-dibromides $CHBr_2 \rightarrow CHO$
s. *10*, 163

α-Halogenacetals from 1,2-dihalogenethers ←
s. *8*, 587

Calcium chloride *$CaCl_2$*

Acetals from 1,1-acoxyhalides $C(OAc)Hal \rightarrow C(OR)_2$
s. *9*, 600

Magnesium *Mg*

O-Labeled alcohols from halides $Hal \rightarrow O^xH$

199. $CH_3Br \rightarrow CH_3O^{18}H$

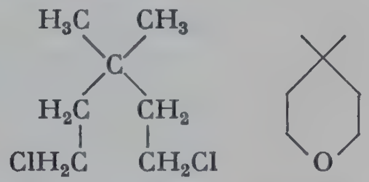
O_2 enriched with O^{18}, obtained by electrolysis of a mixture of H_2SO_4 and water containing H_2O^{18}, introduced into methyl-MgBr in ether → methanol-O^{18}. Y: 50-70% based on the water used. K. B. Wiberg, Am. Soc. *75*, 2665 (1953).

Magnesium oxide *MgO*

Carboxylic acids from carboxylic acid chlorides $COCl \rightarrow COOH$
s. *9*, 402

O-Heterocyclics from dihalides ○

200.



A mixture of 1,5-dichloro-3,3-dimethylpentane (prepn. s. 544), MgO, and water heated 4 hrs. at 250° in a rotating autoclave → 4,4-dimethyltetrahydropyran. Y: 82%. L. Schmerling and J. P. West, Am. Soc. *74*, 2885 (1952).

Mercuric acetate *$(CH_3COO)_2Hg$*

Carboxylic acids from cyclic α-halogenoketones ←
Ring contraction
s. *9*, 326

Zinc chloride/maleic acid s. Maleic acid/zinc chloride ←

Aluminum halides *$AlHal_3$*

Acylation of unreactive alcohols $OH \rightarrow OAc$
s. *8*, 286

Hexamethylenetetramine *$C_6H_{12}N_4$*

Aldehydes from halides – Sommelet reaction $CH_2Hal \rightarrow CHO$
s. *6*, 255; s. a. K. B. Wiberg, Org. Synth., Coll. Vol. III, 811 (1955)

Formamide *$HCONH_2$*

Reaction of halides with formamide ←

Hydrolysis of halides

α-Hydroxy- from α-halogeno-carboxylic acid esters

Carboxylic acids from 1,1,1-trihalides

s. *9*, 327

2-Nitropropane/potassium hydroxide *$(CH_3)_2CH{\cdot}NO_2/KOH$*

Oxo compounds from halides CHHal → CO

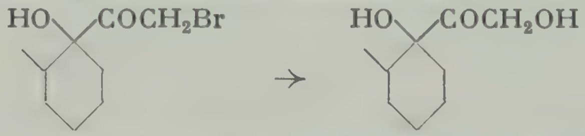
201. $CH_3[CH_2]_9CH_2Br \rightarrow CH_3[CH_2]_9CHO$

A soln. of KOH and 2-nitropropane in 95%-ethanol added dropwise during 45 min. to a refluxing soln. of undecyl bromide in the same solvent, and refluxing continued for 15 min. → undecanal. Y: 85%. F. e. s. S. V. Lieberman, Am. Soc. *77*, 1114 (1955).

Basic ion exchange resin ←

α-Hydroxyketones from α-halogenoketones Hal → OH

202.

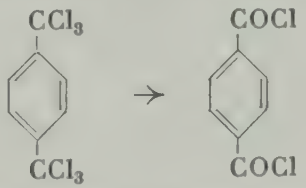


7.8 g. (sol.)-1-bromoacetyl-2-methylcyclohexanol, De-acidite F. F., and aq. methanol refluxed 20 hrs. → 3.9 g. (sol.)-1-glycolloyl-2-methylcyclohexanol. F. e. s. J. D. Billimoria and N. F. Maclagan, Soc. *1954*, 3257.

Maleic acid/zinc chloride ←

Carboxylic acid chlorides from 1,1,1-trichlorides $CCl_3 \rightarrow COCl$

03.



Maleic acid added in small portions with stirring at 135-140° to hexachloro-p-xylene containing a small amount of $ZnCl_2$, heating and stirring continued for 5 min. → terephthaloyl chloride. Y: 95%. N. Rabjohn, Am. Soc. *76*, 5479 (1954).

Stannic chloride *$SnCl_4$*

Hydroperoxides from halides Hal → OOH

s. *6*, 256

Lead oxide *PbO*

Carboxylic acids from halogenhydrins ←

s. *6*, 257

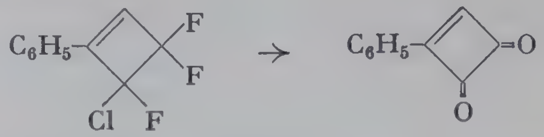
Sulfuric acid *H_2SO_4*

Partial replacement of halogen by hydroxyl Hal → OH

s. *9*, 328

Cyclobutadienoquinones ←

204.



1,1,2-Trifluoro-2-chloro-3-phenylcyclobutene hydrolyzed with 92%-H_2SO_4 at 100° → phenylcyclobutadienoquinone. Y: 75%. E. J. Smutny and J. D. Roberts, Am. Soc. *77*, 3420 (1955).

Carboxylic acids from 1,1,1-trihalides $CHal_3 \rightarrow COOH$
s. *6*, 258

Carboxylic acids from 1,1,1-trichlorides $CCl_3 \rightarrow COOH$
s. *8*, 213; *10*, 451

Selective formation
s. *9*, 329

Reactions with fluoro compounds ←
Carboxylic acid esters from 1,1,1-alkoxydihalides

205. $HCClFCF_2OC_2H_5 \rightarrow HCClFCOOC_2H_5$

96%-H_2SO_4 added dropwise during 30-45 min. with ice-cooling to crude 2-chloro-1,1,2-trifluoroethyl ethyl ether at such a rate that the temp. is maintained at 5-15°, then stirred 2 hrs. at 10° → ethyl chlorofluoroacetate. Y: 65-71%. B. Englund, Org. Synth. *34*, 49 (1954).

Carboxylic acid esters from 1,1,1-trihalides $CHal_3 \rightarrow COOR$
s. *6*, 259

Chlorosulfonic acid/sulfuric acid HSO_3Cl/H_2SO_4

Carboxylic acids from 1,1,1-trihalides $CHal_3 \rightarrow COOH$
s. *6*, 258

Perchloric acid $HClO_4$

Replacement of chlorine by hydroxyl $Cl \rightarrow OH$
s. *6*, 260

Hydrochloric acid HCl

Aminoalcohols from acylaminohalides ←
s. *9*, 330

2-Pyridones from 2-halogenopyridinium salts ←
s. *8*, 287

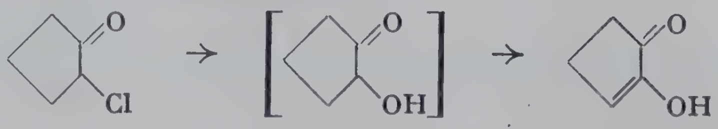
Hydrobromic acid/sulfuric acid HBr/H_2SO_4

Replacement of bromine by hydroxyl $Br \rightarrow OH$
s. *6*, 261

Ferric chloride $FeCl_3$

α-diketones from α-chloroketones ←

206.



2-Chlorocyclopentanone in water heated to 100° with vigorous stirring, then aq. $FeCl_3$ added dropwise, and NH_4-sulfate dissolved in the soln. at 40° → cyclopentane-1,2-dione. Y: 80.5%. H. H. Inhoffen and H. Krämer, B. *87*, 488 (1954).

Sulfur ↓ OC⇅S

Without additional reagents *w.a.r.*

2,4-Thiazolidiones from 4-thiazolidone-2-thiones via 2-alkylmercaptothiazolinium salts C:S → C:O
s. *7*, 305

O-Alkyllactims from lactams ←
s. *7*, 306

Sodium hydride *NaH*

Ethers from p-toluenesulfonic acid esters OH → OR
s. *6*, 262

Sodium hydroxide *NaOH*

Hydroxy compounds from sulfones SO_2R → OH
s. *6*, 484

Methylation of carbohydrates OH → OCH_3
s. *7*, 307

Quinolethers from quinols OH → OR
s. *7*, 192

Alkoxycarboxylic acids from hydroxycarboxylic acids via alkoxycarboxylic acid esters
s. *8*, 288

Potassium hydroxide *KOH*

Selective etherification – Blocking of hydroxyl groups
s. *8*, 289

Ethers from sulfones SO_2R → OR′
s. *9*, 331

Potassium hydroxide/alcohol

Naphthostyrils from cyanosulfonic acids with simultaneous replacement of sulfonic acid groups by hydroxyl SO_3H → OH
s. *7*, 537

Sodium/alcohol *NaOR*

Ethers ROR
s. *9*, 800

from p-toluenesulfonic acid esters
s. *10*, 583

Potassium/alcohol *KOR*

Ketoenolethers from β-diketones $COCH_2CO$ → C(OR):CHCO
O-Alkylation
s. *8*, 290

Potassium carbonate K_2CO_3

Ethers ROR

s. *2*, 272; also partial etherification s. S. R. Gupta and T. R. Seshadri, Soc. *1954*, 3063

Alkali acetate ←

Acetoxy compounds from p-toluenesulfonic acid esters OTs → OAc

Epimerization with Na-acetate s. *6*, 263; s. a. J. Iriarte, G. Rosenkranz, and F. Sondheimer, J. Org. Chem. *20*, 542 (1955); carbohydrates with K-acetate s. L. Vargha, B. *87*, 1351 (1954)

Sodium acetate CH_3COONa

Acetoxy compounds from methylsulfonic acid esters OSO_2CH_3 → OAc

s. *8*, 291

Sodium nitrite/nitric acid s. Nitric acid/sodium nitrite $NaNO_2/HNO_3$

Potassium salt K^+

Peroxides from hydroperoxides R·OOH → R·OO·R′

s. *7*, 308

Pyridine C_5H_5N

Ethers from tosylates and halides via quaternary pyridinium salts ROR

s. *6*, 264

Silver salt Ag^+

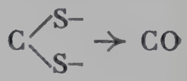
Sulfonium salts as alkylating agents

Carboxylic acid esters from carboxylic acids COOH → COOR

s. *8*, 292

Cadmium carbonate/mercuric chloride $CdCO_3/HgCl_2$

Cleavage of mercaptals



$C\left\langle\begin{matrix}S-\\S-\end{matrix}\right. \rightarrow CO$

s. *2*, 274; s. a. D. J. Cram and M. Cordon, Am. Soc. *77*, 1810 (1955); J. L. Barclay, A. B. Foster, and W. G. Overend, Soc. *1955*, 2505

Acetals from mercaptals $C(SR)_2 \rightarrow C(OR)_2$

s. *8*, 293

Mercuric chloride $HgCl_2$

Ethers from thioethers SR → OR′

s. *7*, 309

Nitric acid/sodium nitrite $HNO_3/NaNO_2$

Diazo oxides from sulfamic acids ←

s. *9*, 332

Phosphorus/hydriodic acid s. Hydriodic acid/phosphorus P/HI

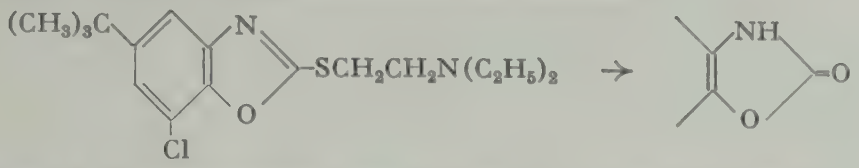
Hydrogen peroxide H_2O_2

Replacement of sulfur by oxygen C:S → C:O

s. *6*, 265

Benzoxazolones from 2-alkylthiobenzoxazoles ←

207.



A soln. of 2-(2′-diethylaminoethylmercapto)-5-*tert*-butyl-7-chlorobenzoxazole (prepn. s. 487) and 30%-H_2O_2 in acetic acid allowed to stand 3 days → 5-*tert*-butyl-7-chlorobenzoxazolone. Y: 74%. L. Katz and M. S. Cohen, J. Org. Chem. *19*, 767 (1954).

Aryltrithiopercarbonic acid esters ←
from bis(triarylthiomethyl) trisulfides
s. *9*, 333

Sulfuric acid *H_2SO_4*

Carbohydrate acetates from carbohydrate sulfuric acid esters ←
s. *6*, 266

Replacement of sulfur by oxygen C:S → C:O
s. *8*, 294

Chlorine *Cl*

s. *6*, 267

Hydrochlorides ←

Alcohols from sulfones $R\cdot SO_2\cdot R' \rightarrow R\cdot OH$
s. *8*, 295

Hydrochloric acid *HCl*

Partial hydrolysis of pyrimidyl thioethers SR → OH
s. *6*, 268

Oxo compounds from thioenolethers ←
s. *7*, 612

Cleavage of sulfonylthioethers ←
s. *7*, 310; *9*, 334

Acetals from sulfurous acid esters CO → C (OR)
s. *9*, 335

Replacement of sulfamido groups by hydroxyl $SO_2NH_2 \rightarrow OH$
s. *7*, 311

Hydriodic acid/phosphorus *HI/P*

α-Aminocarboxylic acids from 5-thiazolidone-2-thiones C
s. *6*, 269

from aldehydes via 5-thiazolidone-2-thiones
Synthesis with addition of 2 C-atoms
s. *9*, 336

Via intermediates *v.i.*

Carboxylic acids from carboxylic acid thioamides $CSNH_2 \rightarrow COOH$
s. *8*, 568

Remaining Elements ↑ OC ⇅ Rem

Without additional reagents *w.a.r.*

Hydroperoxides from Grignard reagents R·MgHal → R·OOH
s. *9*, 337; s. a. Am. Soc. *77*, 6032 (1955)

Sodium salt Na^+

Carboxylic acid esters from carboxylic acids COOH → COOR
Labeled compounds s. *6*, 270

Carbon ↑ OC ⇅ C

Without additional reagents *w.a.r.*

Transacetalization $C(OR)_2 \rightarrow C(OR')_2$
s. *8*, 296

1-Alkoxy-1-acylamines from 1-acoxy-1-acylamines OAc → OR
s. *8*, 297

Cleavage of β-hydroxycarboxylic acid esters ←
s. *8*, 298

Transesterification COOR → COOR′
s. *7*, 312

Enolesters from enolethers with rearrangement ←
s. *7*, 313

Orthoformic acid esters – Transesterification $HC(OR)_3$
s. *7*, 314

Boric acid esters $B(OR)_3$
s. *7*, 315

Transesterification ←
Titanic acid esters s. *9*, 338 **Mixed dialkyl phosphites** s. *9*, 339

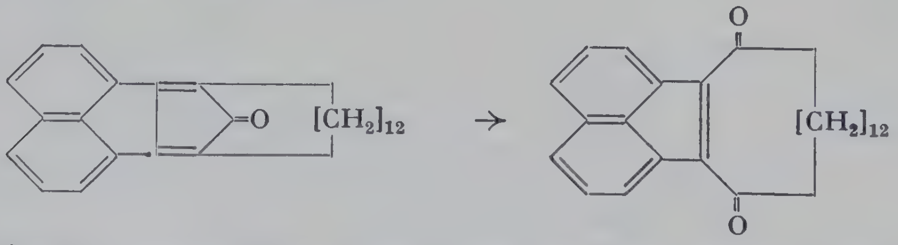
Selenenic acid esters SeOR
s. *7*, 316

1,2,4-Trioxolones from ethylene derivatives ○
s. *9*, 340

Irradiation ←

Oxidative cyclone ring opening C

208.



Air bubbled by means of a sintered glass disperser through a soln. of 8-19-dodecahydro-7,20-methanocyclohexadeca[1,2-a]acenaphthylen-21-one (prepn. s. 579) in isoöctane with irradiation by a sun lamp until the bright red soln. becomes yellow → 7-20-tetradecahydrocyclohexadeca-

[1.2-a]acenaphthylene-7.20-dione (startg. m. f. 302). Y: 97%. F. e. s. C. F. H. Allen and J. A. Van Allan, J. Org. Chem. *18*, 882 (1953).

Electrolysis ↯

1-Alkoxy-1-acylamines $COOH \rightarrow OR$
from α-acylaminocarboxylic acids
Degradation with loss of 1 C-atom
s. *8*, 299

Sodium *Na*

Transesterification $COOR \rightarrow COOR'$
s. *7*, 317

Sodium hydroxide *NaOH*

Ketones from nitroalcohols ←
s. *6*, 271

Carboxylic acids from trihalogenomethyl ketones $COCHal_3 \rightarrow COOH$
s. *7*, 320

Thiophene 1,1-dioxide ring opening ↺
s. *8*, 868

Potassium hydroxide *KOH*

Transetherification of activated ethers $OR \rightarrow OR'$
s. *6*, 272

Carboxylic acids from methyl ketones $COCH_3 \rightarrow COOH$
via pyridinium salts
Degradation with loss of 1 C-atom
s. *8*, 300

Carboxylic acids $CH{:}CHCOOH \rightarrow COOH + CH_3COOH$
from α,β-ethylenecarboxylic acid esters
via α,β-ethylenecarboxylic acids
Degradation of carboxylic acids with loss of 2 C-atoms
s. *8*, 301

1,1-Alkoxynitro compounds and carboxylic acids ←
from enedinitro compounds
s. *7*, 319

Carboxylic acids from $CH(ONO_2)CHal_3 \rightarrow COOH$
α-(trihalogenomethyl)nitric acid esters
s. *7*, 318

Carboxylic acid esters $COCHal_3 \rightarrow COOR$
from trihalogenomethyl ketones
s. *8*, 302

Potassium hydroxide/alcohol

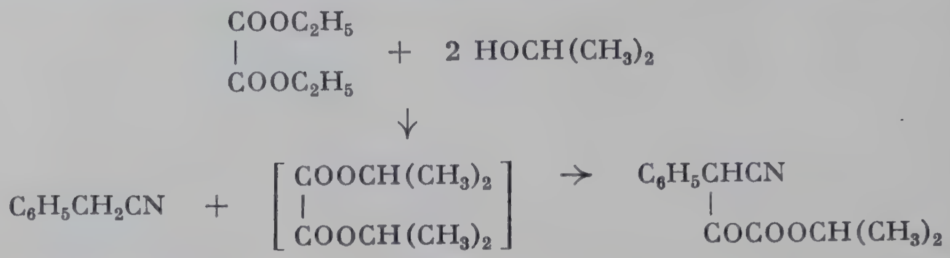
Hydrolytic cleavage of the carbon chain ←
s. *9*, 797

Sodium/alcohol *NaOR*

Transetherification with simultaneous transesterification ←
s. *7*, 743

Oxalic ester synthesis with transesterification COOR → COOR′

209.



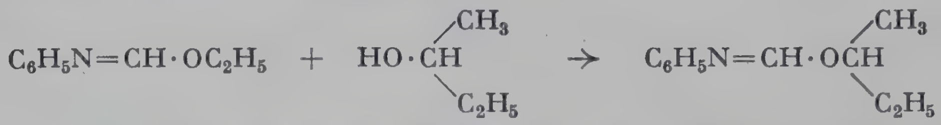
$$\begin{array}{c}COOC_2H_5\\|\\COOC_2H_5\end{array} + 2\,HOCH(CH_3)_2 \;\downarrow\; C_6H_5CH_2CN + \left[\begin{array}{l}COOCH(CH_3)_2\\|\\COOCH(CH_3)_2\end{array}\right] \rightarrow \begin{array}{l}C_6H_5CHCN\\\quad|\\\quad COCOOCH(CH_3)_2\end{array}$$

Diethyl oxalate added to a soln. of Na in excess isopropanol, after the exothermic reaction has subsided benzyl cyanide added, and allowed to stand 24 hrs. → isopropyl phenylcyanopyruvate. Y: 80%. F. e., also transesterification without condensation, s. J. Klosa, Arch. Pharm. *285*, 364 (1952).

Partial transesterification
s. *9*, 341

Transesterification of iminoesters C(:NR)COR′ → C(:NR)COR″

210.



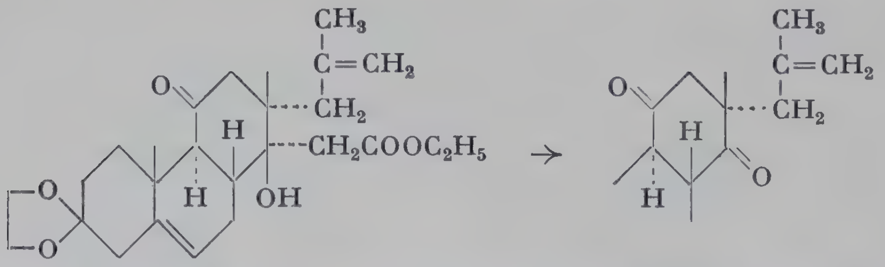
$$C_6H_5N{=}CH\cdot OC_2H_5 + HO\cdot CH\begin{array}{l}\diagup CH_3\\ \diagdown C_2H_5\end{array} \rightarrow C_6H_5N{=}CH\cdot OCH\begin{array}{l}\diagup CH_3\\ \diagdown C_2H_5\end{array}$$

Ethyl N-phenylformimidate added to a soln. of Na in excess *sec*-butanol and heated with distillation of the resulting ethanol → *sec*-butyl N-phenylformimidate. Y: 85%. F. e. s. R. M. Roberts, T. D. Higgins, Jr., and P. R. Noyes, Am. Soc. *77*, 3801 (1955).

Potassium/alcohol *KOR*

Hydrolytic cleavage of the carbon chain C(OH)CH₂COOR → CO
Ketones from β-hydroxycarboxylic acid esters

211.



A soln. of 2β,4b-dimethyl-1-carbethoxymethyl-2-methallyl-7-ethylenedioxy-1,2,3,4,4aα,4b,5,6,7,8,10,10aβ-dodecahydrophenanthren-1β-ol-4-one in dry benzene treated with a 1 *M* soln. of K in *tert*-butanol, and the product isolated after 5 min. → diketone. Y: 75%. Also with the stereoisomer s. G. E. Arth et al., Am. Soc. *76*, 1715 (1954); with 20%-NaOH soln. cf. G. N. Walker, Am. Soc. *75*, 3387 (1953).

Potassium tert-butoxide *$KOC(CH_3)_3$*

Autoxidation ←

12. $C_6H_5COCH(CH_3)_2 \rightarrow C_6H_5COOH$

The autoxidation of several aldehydes, ketones, and esters having α-H is extremely rapid in the presence of *tert*-butoxide ion.—E:Isobutyrophenone in a soln. of K in *tert*-butanol allowed to react with O_2, and the product isolated after 7 min. → benzoic acid. Y: 75%. F. e. s. W. von E. Doering and R. M. Haines, Am. Soc. *76*, 482 (1954).

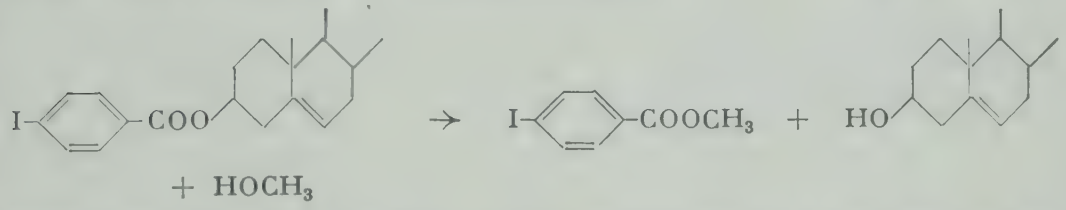
Sodium hydrogen carbonate *$NaHCO_3$*

Carboxylic acids from trihalogenomethyl ketones $COCCl_3 \rightarrow COOH$
s. *7*, 320

Potassium cyanide *KCN*

Non-aqueous buffering – Transesterification COOR → COOR′

13.



KCN in abs. methanol added to a soln. of cholesteryl p-iodobenzoate in dry benzene, and refluxed 18 hrs. → methyl p-iodobenzoate (Y: 85%) and cholesterol (Y: 100%). F. e. s. Q. R. Petersen, Am. Soc. 77, 1743 (1955).

Ammonia *NH_3*

Degradation of carbohydrates with loss of 1 C-atom via mercaptals and 1,1-disulfones ←
s. *9*, 342; s. a. L. Hough and T. J. Taylor, Soc. *1955*, 1212

Benzyldimethylamine *$C_6H_5CH_2N(CH_3)_2$*

Transesterification COOR → COOR′
s. *9*, 343

Pyridine *C_5H_5N*

1,1-Di(acylperoxy) compounds from hydroxy hydroperoxy peroxides ←
s. *6*, 273

Cyclic carbonates ○
s. *10*, 381

Cupric acetate *$(CH_3COO)_2Cu$*

Reactions with isopropenyl acetate ←
Acetylation, enol acetates
Acetylamines
s. *6*, 208

Fehling solution ←

Aldehydes from hydrobenzoins $ArCH(OH)CH(OH)Ar \rightarrow 2ArCHO$

s. *9*, 732

Barium hydroxide/oxygen s. Oxygen/barium hydroxide $Ba(OH)_2/O_2$

Zinc/ozone s. Ozone/zinc Zn/O_3

Mercuric acetate $(CH_3COO)_2Hg$

Carboxylic acid esters from carboxylic acids $COOH \rightarrow COOR$

Transacylation

s. *6*, 274

Aluminum alkoxide $Al(OR)_3$

Transesterification $COOR \rightarrow COOR'$

Optically active α-aminocarboxylic acid esters

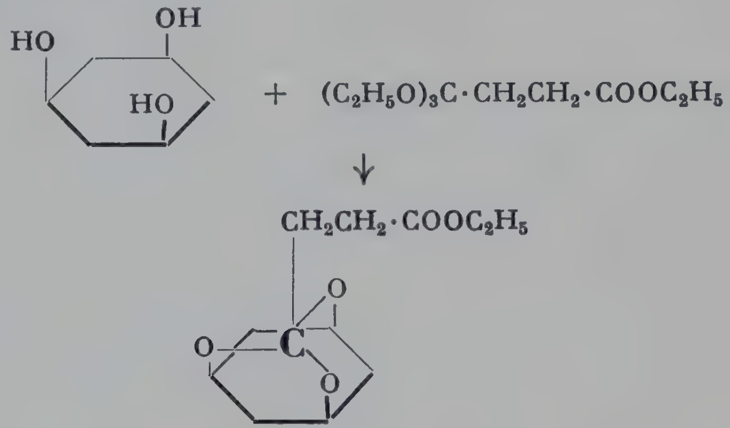
s. *9*, 344; transesterification s. a. K. W. Rosenmund, F. Zymalkowski, and E. Gussow, Arch. Pharm. *286*, 324 (1953)

Boron fluoride BF_3

Trans(orthoesterification) ←

Protection of carboxyl groups

214.

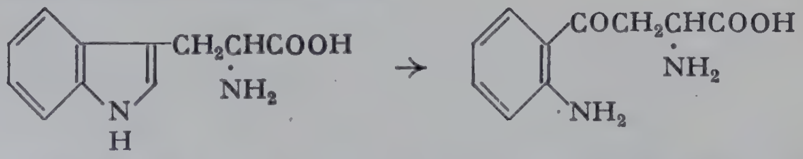


2,4,10-Trioxaadamantanes. *cis*-Phloroglucitol added to a soln. of tetraethyl semiorthosuccinate in abs. ethanol, a few bubbles of BF_3 introduced, then allowed to stand 24 hrs. at room temp. with frequent shaking → ethyl 2-(2,4,10-trioxaadamantyl-3)-propionate. Y: 71%.— Only the normal ester group of the product reacts with organometallic compounds to form ketones and tert. alcohols. H. Stetter and K. H. Steinacker, B. *87*, 205 (1954).

Pseudomonas extract ←

Bioöxidative indole ring opening

215.



Pseudomonas extract and 1 drop of n-butyl phosphate (to prevent foaming) added to a soln. of L-tryptophan in 0.04 *M* K-phosphate buffer (pH 8.0), and shaken for vigorous aeration with addition of 2 *N* KOH to maintain the pH at ca. 7.8 until the reaction is complete after ca. 3 hrs. → L-kynurenine. Y: 50-63%. O. Hayaishi, Biochem. Prep. *3*, 108 (1953).

Nitrobenzene *$C_6H_5NO_2$*

Aldehydes by oxidative degradation of side chains CHO

s. *7*, 321

Carboxylic acid esters *RCOOR′*

Titanium-, zirconium-, and hafnium alkoxides by transesterification ←

16. $[(CH_3)_2CHO]_4Zr + 4\ (CH_3)_3C\cdot OCOCH_3 \rightarrow [(CH_3)_3C\cdot O]_4Zr$

Zirconium isopropoxide refluxed with *tert*-butyl acetate under a column for ca. 2 hrs. → zirconium *tert*-butoxide. Y: 80%. F. e. s. R. C. Mehrotra, Am. Soc. *76*, 2266 (1954).

Peracetic acid/p-toluenesulfonic acid *$CH_3COO_2H/TsOH$*

s. p-Toluenesulfonic acid/peracetic acid

Perbenzoic acid *$C_6H_5COO_2H$*

Alcohols from ketones COR → OH

Oxidative degradation – Retention of configuration

s. *7*, 322

Acetyl chloride *CH_3COCl*

Acoxy compounds from triphenylmethyl ethers OTr → OAc

s. *7*, 323

Stannic chloride *$SnCl_4$*

Glycosides OAc → OR

β-Glucopyranosides s. *9*, 345

Lead tetraacetate *$(CH_3COO)_4Pb$*

Oxidative cleavage – Oxo compounds from glycols CO

s. *6*, 275; s. a. F. J. Wolf and J. Weijlard, Org. Synth. *35*, 18 (1955)

Degradation

of carbohydrates
s. *9*, 346

Ketones from glycols ←
s. *6*, 316; *8*, 53

Oxidative cleavage ←

of α-hydroxyketones and α-ketocarboxylic acids

α-Diketones from α-hydroxyketones

s. *9*, 347

Hydrazine *$H_2N\cdot NH_2$*

Degradation of carbohydrates with loss of 1 C-atom via mercaptals and 1,1-disulfones CHO

s. *7*, 324

Sodium azide NaN_3
Ketones from 1,1-diarylethylenes CO
Schmidt reaction – Migration aptitude
s. *6*, 276

Vanadium pentoxide/nitric acid V_2O_5/HNO_3
o-Dicarboxylic acids from carboxylic acids C
Cyclic ketones from carboxylic acids
Oxidative ring opening
s. *7*, 325

Sodium bismuthate $NaBiO_3$
Oxidative cleavage and degradation ←
Oxo compounds from glycols, acyloins,
and α-hydroxycarboxylic acids
s. *6*, 277; steroid derivatevs s. a. H. L. Herzog et al., Am. Soc. *77*, 4781 (1955); cf. A. R. Battersby and R. Binks, Soc. *1955*, 2896

Oxygen O_2
Hydroxynaphthoquinones ←
s. *6*, 278

Oxygen/barium hydroxide $O_2/Ba(OH)_2$
Spengler and Pfannenstiel COOH
oxidative degradation of carbohydrates
s. *9*, 348

Ozone/zinc O_3/Zn
Aldehydes from ethylene derivatives CHO
Degradation of carbohydrates
s. *6*, 279

with loss of 1 C-atom
s. *6*, 282

Oxo compounds from ethylene derivatives CO
with protection of a carbon-carbon double bond
s. *6*, 280; protection of carbon-carbon double bonds s. a. L. F. Fieser, Org. Synth. *35*, 43 (1955)

Ozone/hydrogen peroxide O_3/H_2O_2
Carboxylic acids from ethylene derivatives COOH
s. *9*, 349

Oxidative ring opening C
s. *6*, 281; *8*, 945; *9*, 350

Hydrogen peroxide/sodium hydroxide $H_2O_2/NaOH$
o-Aminocarboxylic acids from isatins
s. *8*, 303

Hydrogen peroxide/potassium hydroxide H_2O_2/KOH
Oxidative tropolone ring opening
s. *9*, 351

Hydrogen peroxide/perchloric acid *$H_2O_2/HClO_4$*
Cleavage of α-diketones to carboxylic acids RCOCOR → 2 RCOOH
s. *8*, 304

Sodium hydrogen sulfate *$NaHSO_4$*
Transetherification OR → OR′
s. *7*, 326

p-Toluenesulfonic acid *TsOH*
Enol acetates from ketones ←
s. *8*, 307

γ-Hydroxy-α,β-ethyleneketones ←
from α,β-ethyleneketones via (dien)olesters
Introduction of hydroxyl into the 11α-position of steroids
s. *8*, 305

β-Ketocarboxylic acid esters from 6-keto-1,3-diox-4-enes ⊂
s. *9*, 212

Partial transdioxolanation ←
Protection of keto groups – Alcohols from ketones
s. *9*, 352; partial transdioxolanation s. a. F. Sondheimer, M. Velasco, and G. Rosenkranz, Am. Soc. *77*, 192 (1955)

p-Toluenesulfonic acid/peracetic acid *$TsOH/CH_3COO_2H$*
Hydroxy compounds from ketones COR → OH
Oxidative degradation
s. *6*, 283

α-Naphthalenesulfonic acid ←
Transacetalization ←
s. *6*, 284; *8*, 306

Sulfuric acid *H_2SO_4*
Sym. ethers from carboxylic acids 2 RCOOH → ROR
via carbonium ions
Elimination of carbon monoxide

17. $2\,(p\text{-}ClC_6H_4)_2CHCOOH \rightarrow 2\,(p\text{-}ClC_6H_4)_2\overset{+}{C}H \rightarrow (p\text{-}ClC_6H_4)_2CHOCH(C_6H_4Cl\text{-}p)_2$

Bis-(p-chlorophenyl)acetic acid added to 100%-H_2SO_4, stirred 40 min., then poured onto crushed ice → bis-(p.p′-dichlorodiphenylmethyl) ether. Y: 88%. C. M. Welch and H. A. Smith, Am. Soc. *75*, 1412 (1953).

Transacetalization ←

18. $ClCH_2CH(OCH_3)_2 + 2\ HOC_4H_9\text{-}n \rightarrow ClCH_2CH(OC_4H_9\text{-}n)_2$

A mixture of dimethyl chloroacetal, n-butanol, and H_2SO_4 heated until the theoretical quantity of methanol has been collected → dibutyl chloroacetal. Y: 84%. G. Eglinton et al., Soc. *1954*, 1860.

Acoxy compounds from acetals ←
s. *9*, 353

Enol acetates from ketones ←
s. *8*, 307

Ketone-enolester exchange ←
s. *8*, 308

Transacylation of enolesters OR → OR′
s. *8*, 309

Transesterification COOR → COOR′
s. *4*, 263; s. a. J. Cason, K. L. Rinehart, Jr., and S. D. Thornton, Jr., J. Org. Chem. *18*, 1594 (1953)

Carboxylic acids and methyl ketones from acylmalonic acid esters ←
s. *6*, 285

Ketones from iminonitriles C(CN)C:NH → CHCO
s. *10*, 561

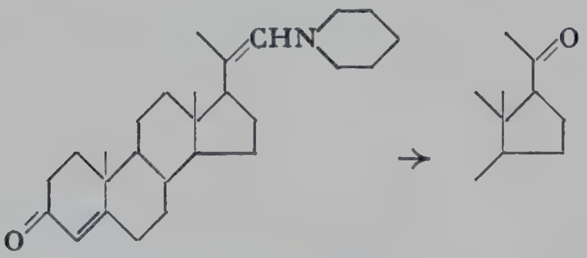
Selenium dioxide SeO_2

Oxidation and elimination of side chains ←
s. *8*, 310

Sodium dichromate/acetic acid $Na_2Cr_2O_7/CH_3COOH$

Ketones from aminomethylene compounds
Degradation with loss of 1 C-atom C:CHN< → CO

219.



A soln. of 22-(N-piperidyl)bisnor-4,20(22)-choladien-3-one in benzene added during 1 hr. below 5° to a soln. of Na-dichromate in glacial acetic acid-benzene, stirring continued for 2 hrs., methanol added, and stirred 30 min. → progesterone. Y: 88-96.5%.—This is the final step of a synthesis of progesterone from ergosterol in an over-all yield of 37%. The synthesis can be performed without isolation of the enamine. F. steps s. D. A. Shepherd et al., Am. Soc. *77*, 1212 (1955).

Chromic acid CrO_3

Oxidative degradation CO
s. *8*, 311

Phenanthridones from phenanthridines ←
s. *9*, 354

Hypohalites *$HalO^-$*

Carboxylic acids from ketones COR → COOH

Oxidative degradation

s. *6*, 286

1,3-Cyclohexanedione ring opening C

s. *7*, 327

Perchloric acid *$HClO_4$*

Ketones from alcohols by cleavage via peroxides CO

Migration aptitude

s. *7*, 328

Perchloric acid/hydrogen peroxide *$HClO_4/H_2O_2$*

s. Hydrogen peroxide/perchloric acid

Periodate *IO_4^-*

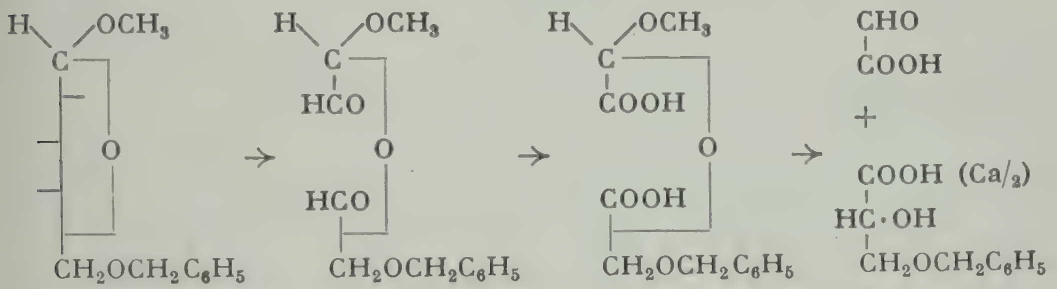
Oxidative degradation to aldehydes CHO

s. *8*, 312

Carboxylic acids via aldehydes by oxidative cleavage COOH

Cleavage of acetals

220.



Methyl 6-O-benzyl-α-D-galactopyranoside added to cooled aq. Na-metaperiodate, allowed to stand at room temp. overnight, to the aq. soln. of the resulting dialdehyde a soln. of iodine in aq. KI added followed immediately by a buffer prepared from K-carbonate, $KHCO_3$, and water, swirled, left 2 hrs. in the dark at room temp. with occasional shaking, cautiously treated with 10 *N* H_2SO_4, excess iodine reduced with Na-thiosulfate, the aq. soln. of the resulting dicarboxylic acid heated 2 hrs. on a steam bath to hydrolyze the acetal structure, and the resulting 3-O-benzyl-D-glyceric acid isolated as Ca-salt with Ca-hydroxide → Ca-3-O-benzyl-D-glycerate. Y: 60%.–Oxidation of the dialdehyde with Br was unsuccessful. C. E. Ballou and H. O. L. Fischer, Am. Soc. *76*, 3188 (1954).

Pyran ring from cyclohexane ring ←

s. *6*, 287

Triethylamine hydrochloride *$(CH_3)_3N,HCl$*

Transetherification ←

Ethers from carboxylic acid esters

3-Alkoxyfurans s. *6*, 288

Hydrochloric acid *HCl*

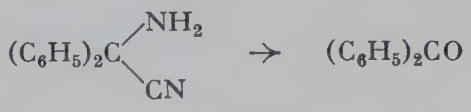
Carbohydrates and glycosides from isopropylidene derivatives ←
s. *8*, 313

Transacetalization ←
s. *10*, 483

Hydrolytic cleavage of the carbon chain C·C → C·OH
s. *8*, 314

Ketones from α-aminonitriles $C(CN)NH_2 \rightarrow CO$

221.

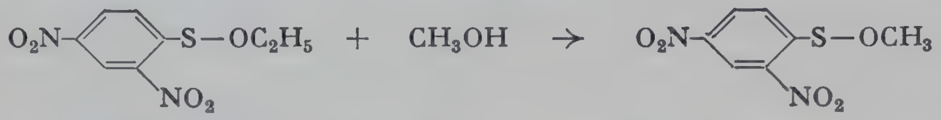


$(C_6H_5)_2C(NH_2)(CN) \rightarrow (C_6H_5)_2CO$

Diphenylglycinonitrile (prepn. s. 531) heated with concd. HCl at 80° for 30 min. → benzophenone. Y: 80%. H. M. Woodburn and L. B. Lathroum, J. Org. Chem. *19*, 285 (1954).

Transesterification of sulfenic acid esters ·S·OR → ·S·OR′

222.



A gentle stream of HCl passed at 30° into a soln. of ethyl 2,4-dinitrobenzenesulfenate in abs. methanol, finally refluxed 2 min. → methyl 2,4-dinitrobenzenesulfenate. Y: 84%.—Reverse conversion, Y: 83%. F. e. s. N. Kharasch, D. P. McQuarrie, and C. M. Buess, Am. Soc. *75*, 2658 (1953).

Tetrahydrofurans ○
s. *7*, 329

4-Imidazolidone ring opening C
s. *8*, 315

Enediollactones ←
s. *7*, 330

Hydrobromic acid *HBr*

2-Thiohydantoin ring opening C
s. *8*, 475

Potassium permanganate *$KMnO_4$*

Oxidative degradation to ketones CO
s. *8*, 316

α-Hydroxyketones from α,β-ethylenenitriles C:C·CN → C(OH)CO
17α-Hydroxy-20-ketosteroids s. *8*, 317

Aldonic acids from glycals ←
s. *6*, 322

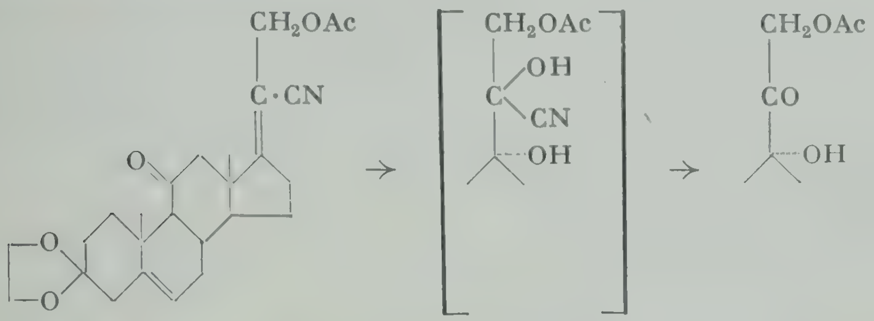
Oxidative ring contraction ←
s. *8*, 318

3-Hydroxyphthalimidines from isoquinolines ←
s. *6*, 289

Potassium permanganate/piperidine/acetic acid $KMnO_4/C_5H_{11}N/CH_3COOH$

α-Hydroxyketones from α,β-ethylenenitriles C:C·CN → C(OH)CO
17α-Hydroxy-20-ketosteroids

223.



Improved procedure. Powdered $KMnO_4$ added to an ice-cold stirred soln. of $\Delta^{5,17}$-20-cyano-3-ethylenedioxypregnadiene-21-ol-11-one acetate in acetone containing piperidine, stirred 1.5 hrs. at 0°, allowed to warm to room temp. during 30 min., treated with acetic acid in acetone to maintain a pH of ca. 9, stirred 1.5 hrs. at room temp., then treated with chloroform, aq. $NaHSO_3$, and sufficient 1 *N* H_2SO_4 to reduce all the MnO_2, the crude product stirred 1 hr. at room temp. in chloroform with aq. K-carbonate → 3-ethylenedioxycortisone acetate. Y: 79%. G. I. Poos et al., Am. Soc. *76*, 5031 (1954); f. e., on a larger scale, s. Am. Soc. *77*, 196 (1955).

Potassium permanganate/pyridine $KMnO_4/C_5H_5N$

Carboxylic acids from ethylene derivatives CH:C → COOH
s. *6*, 135

Via intermediates *v.i.*

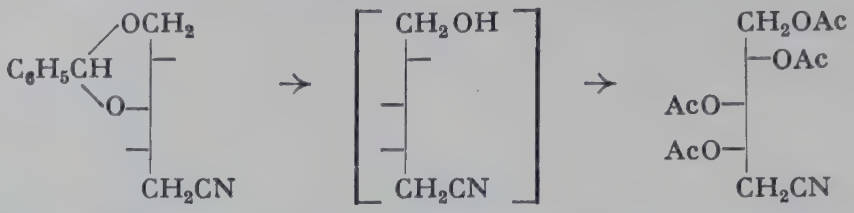
Transacetalization ←
Ethylidene from benzylidene derivatives of carbohydrates
s. *9*, 355

Aldehydes $CH(CONHNH_2)_2$ → CHO
from α-dicarboxylic acid hydrazides
via 1,1-dicarbalkoxyamines
s. *8*, 319

Ketones from barbituric acids ←
via carboxylic acids and hydrazones
Japp-Klingemann reaction
s. *6*, 290

Acoxynitriles from cyanoacetals ←

224.



4,6-Benzylidene-2-desoxy-L-galactononitrile (prepn. s. 583) and 20%-acetic acid heated with distillation of a benzaldehyde-acetic acid mixture and dropwise addition of 10%-acetic acid until after ca. 30 min. no more benzaldehyde is formed, the crude product allowed to stand 2 days at room temp. with acetic anhydride in pyridine → 3,4,5,6-tetraacetyl-2-desoxy-L-galactononitrile. Y: 91%. F. e. s. R. Grewe and H. Pachaly, B. *87*, 46 (1954).

Transacylation of glycosides OAc → OAc′
s. 6, 291

Elimination

Hydrogen ↑ OC ⇑ H

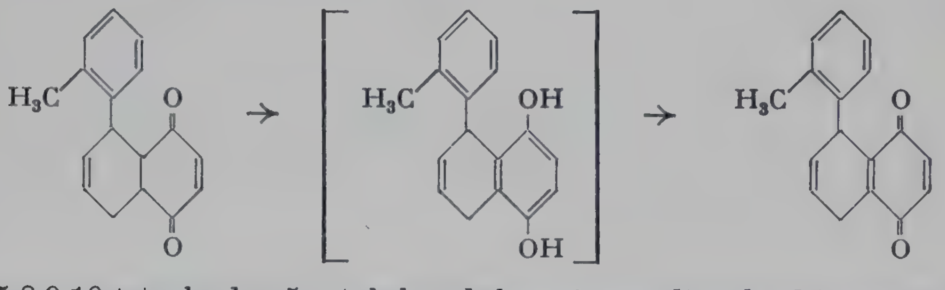
Potassium alkoxide *KOR*

Oppenauer oxidation CH(OH) → CO
Ketones from sec. alcohols
s. *7*, 331

Sodium nitrite *$NaNO_2$*

Quinones from enediones via quinols ←

225.



2 g. 5,8,9,10-tetrahydro-5-o-tolylnaphthoquinone dissolved in acetic acid at 100°, then aq. $NaNO_2$ added → 1.8 g. 5,8-dihydro-5-o-tolylnaphtho-1,4-quinone. E. A. Braude, J. S. Fawcett, and A. A. Webb, Soc. *1954*, 1049.

Copper *Cu*

Carboxylic acids from alcohols via aldehydes CH_2OH → COOH
s. *6*, 292

Silver oxide/sodium sulfate *Ag_2O/Na_2SO_4*

Quinones from quinols ←
s. *8*, 320

Silver oxide/magnesium sulfate $Ag_2O/MgSO_4$
s. *9*, 256

Cupric hydroxide/acetic acid $Cu(OH)_2/CH_3COOH$
Benzils from hydrobenzoins $CH(OH)CH(OH) \rightarrow COCO$
s. *9*, 732

Cupric acetate $(CH_3COO)_2Cu$
Osones from carbohydrates $CH(OH)CO \rightarrow COCO$
s. *9*, 356

Cupric acetate/ammonium nitrate $(CH_3COO)_2Cu/NH_4NO_3$
Benzils from benzoins
s. *5*, 220; s. a. J. H. Biel et al., Am. Soc. *77*, 2250 (1955)

Mercuric oxide HgO
Quinones from quinols ←
s. *8*, 321

Aluminum isopropoxide $Al(OR)_3$
Oppenauer oxidation $CH(OH) \rightarrow CO$
Ketones from sec. alcohols
with simultaneous migration of a carbon-carbon double bond
s. *2*, 286; s. a. D. A. Shepherd et al., Am. Soc. *77*, 1212 (1955); F. Sondheimer et al., Am. Soc. *77*, 4145 (1955); J. F. Eastham and R. Teranishi, Org. Synth. *35*, 39 (1955); 17(20)-en-20-acetaminosteroids s. H. Ruschig et al., B. *88*, 883 (1955)

Oppenauer oxidation and Meerwein-Ponndorf reduction ←
Lactols from diols and diketones
s. *7*, 332

Thallous alkoxide $TlOR$
Benzils from benzoins $CH(OH)CO \rightarrow COCO$
s. *9*, 357

Thallous alkoxide/nitrobenzene $TlOR/C_6H_5NO_2$
s. *9*, 358

Quinones ←
Disproportionation ←
Quinolquinones s. *8*, 322

Acetobacter suboxydans ←
Carbohydrates from polyalcohols ←
Biochemical oxidation
s. *6*, 293

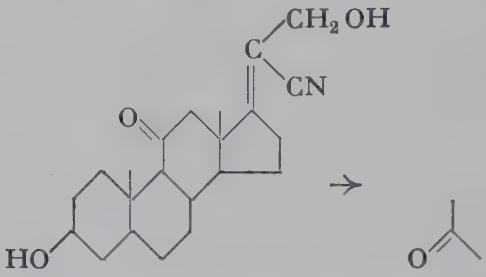
N-Bromoacetamide *$CH_3CONHBr$*

Ketones from sec. alcohols CH(OH) → CO

Partial oxidation

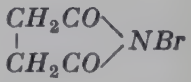
s. *7*, 333; *8*, 323; s. a. M. D. Soffer and M. A. Jevnik, Am. Soc. *77*, 1003 (1955); in tert-butanol and pyridine s. a. J. A. Hogg et al., Am. Soc. *77*, 4438 (1955)

226.



Selective oxidation. 20-Cyano-3α,21-dihydroxy-17-pregnen-11-one added to a soln. of N-bromoacetamide in methanol-water containing pyridine, stirred overnight at room temp. protected from light, then allyl alcohol added to decompose excess N-bromoacetamide → 20-cyano-21-hydroxy-17-pregnene-3,11-dione. Y: 96.5%. R. E. Jones and F. W. Kocher, Am. Soc. *76*, 3682 (1954).

N-Bromosuccinimide



$$\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \!\!> NBr$$

Selective oxidation

s. *6*, 294

β-Bromo-α-ketocarboxylic acid esters and α-ketocarboxylic acid esters from α-hydroxycarboxylic acid esters ←

α-Bromoketones from sec. alcohols

227. $C_6H_5CH_2CH(OH)COOC_2H_5 \rightarrow C_6H_5CHBrCOCOOC_2H_5$

$C_6H_5CH(OH)COOC_2H_5 \rightarrow C_6H_5COCOOC_2H_5$

Slightly less than 2 moles N-bromosuccinimide added to a soln. of ethyl DL-α-hydroxyhydrocinnamate in CCl_4, and refluxed 5 hrs. → ethyl DL-β-bromophenylpyruvate. Y: 71%.—Similarly with DL-phenylmethylcarbinol and 2 moles N-bromosuccinimide → phenacyl bromide. Y: 44.2%.—Ethyl mandelate with 1 mole N-bromosuccinimide during 8 hrs. → ethyl phenylglyoxylate. Y: 78.5%. F. β-bromo-α-ketocarboxylic acid esters s. P. F. Kruse, Jr., N. Geurkink, and K. L. Grist, Am. Soc. *76*, 5796 (1954).

Lead dioxide *PbO_2*

Sensitive quinones from quinols ←

Active lead dioxide s. *7*, 334

Lead tetraacetate *$(CH_3COO)_4Pb$*

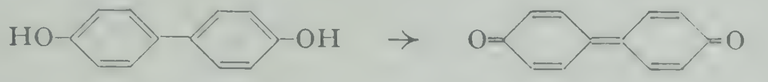
α-Diketones from α-hydroxyketones CH(OH) → CO

s. *9*, 347

α-Keto-
from α-hydroxy-carboxylic acid esters $CH(OH)COOR \rightarrow COCOOR$
s. *9*, 359

Extended quinones ←

228.



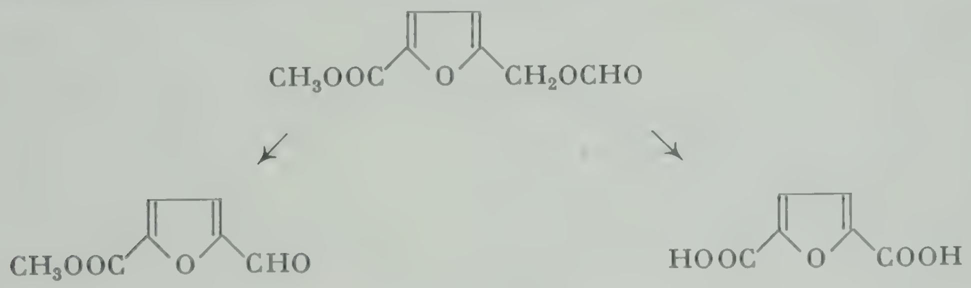
A supersatd. soln. of 4,4′-dihydroxydiphenyl in acetic acid added quickly at 30° to a suspension of Pb-tetraacetate in acetic acid, and kept at room temp. overnight → diphenoquinone. Y: ca. 75%. B. R. Brown and A. R. Todd, Soc. *1954*, 1280.

Benzoxazoles from azomethines ○
s. *6*, 503

Nitrogen dioxide *NO_2*
Aldehydes from prim. alcohols $CH_2OH \rightarrow CHO$
s. *1*, 160; s. a. B. O. Field and J. Grundy, Soc. *1955*, 1110

Nitric acid *HNO_3*
Aldehydes and carboxylic acids from formoxy compounds ←

229.



60 g. 5-carbomethoxyfurfuryl formate 45 g.

140 c.c. 65%-HNO_3. and 120 c.c. water heated cautiously until reaction starts, then ice-cooled, and the reaction allowed to continue slowly for 1 hr. → methyl 5-formylfuran-2-carboxylate. Y: 74%.

171 c.c. 65%-HNO_3, and 90 c.c. water heated cautiously until reaction starts, after the vigorous reaction has subsided allowed to stand without cooling for 4 hrs., then refluxed 0.5 hrs. → furan-2,5-dicarboxylic acid. Y: 79%.

O. Moldenhauer et al., A. *580*, 182 (1953).

Bismuth trioxide and carbonate ←
α-Diketones from acyloins $CH(OH)CO \rightarrow COCO$
s. *7*, 335

Oxygen *O_2*
Benzils from enediols $C(OH){:}C(OH) \rightarrow COCO$
s. *7*, 336

Hydrogen peroxide H_2O_2

Flavonols from chalcones – Algar-Flynn oxidation ○

s. *1*, 245; *4*, 272; flavonol-6-carboxylic acids s. D. N. Shah, S. K. Parikh, and N. M. Shah, Am. Soc. *77*, 2223 (1955)

Selenium dioxide SeO_2

Aldehydes from prim. alcohols $CH_2OH \rightarrow CHO$

s. *7*, 337

o-Aldehydes from diols via cyclic selenous acid esters

s. *7*, 338

3-Aroylflavones via aroyl-o-hydroxybenzoylstyrenes ○

2-Ethylene-1,3-diketones from β-diketones

s. *7*, 339; ring closure s. a. A. Schönberg, N. Badran, and N. A. Starkowsky, Am. Soc. *77*, 5390 (1955)

Copper-cobalt-chromium-asbestos ←

Aldehydes from prim. alcohols $CH_2OH \rightarrow CHO$

s. *8*, 324

Potassium chromate/sodium acetate K_2CrO_4/CH_3COONa

Ketones from sec. alcohols $CH(OH) \rightarrow CO$

Partial oxidation

Steroids s. *7*, 340

Sodium dichromate/acetic acid $Na_2Cr_2O_7/CH_3COOH$

Ketones from sec. alcohols $CH(OH) \rightarrow CO$

s. *9*, 360; s. a. L. F. Fieser, Org. Synth. *35*, 43 (1955)

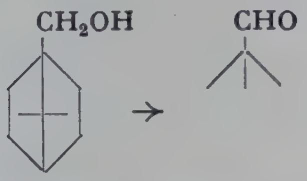
Ketones from acoxy compounds $CH(OAc) \rightarrow CO$

s. *9*, 361

Potassium dichromate/acetic acid $K_2Cr_2O_7/CH_3COOH$

Aldehydes from prim. alcohols $CH_2OH \rightarrow CHO$

230.



A soln. of 10-hydroxycamphane in glacial acetic acid treated with K-dichromate, shaken 1 hr. at 80-90°, and the product isolated as the semicarbazone → apocamphane-1-carboxaldehyde semicarbazone. Y: 81%. W. v. E. Doering et al., Am. Soc. *74*, 3000 (1952).

Chromic acid CrO_3

Ketones from sec. alcohols $CH(OH) \rightarrow CO$

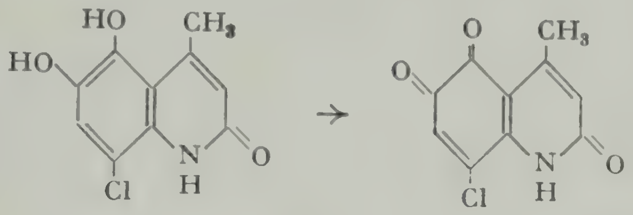
with protection of carbon-carbon double bonds

s. *9*, 362

α,β-Ethyleneketones from 1,3-diols ←
s. *6*, 295

Quinones from quinols ←

231.



o-Quinones. An aq. soln. of CrO_3 added all at once to a suspension of 4-methyl-5,6-dihydroxy-8-chlorocarbostyril → 4-methyl-8-chlorocarbostyril-5,6-quinone. Y: 96%. R. R. Holmes et al., Am. Soc. *76*, 2400 (1954).

Chromic acid-pyridine complex *CrO_3-C_5H_5N*

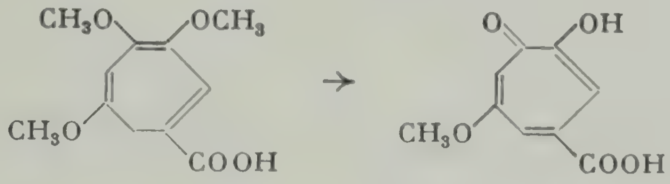
Oxo compounds from alcohols CH(OH) → CO
s. *8*, 325; ketoaldehydes s. Am. Soc. *77*, 1026 (1955)

Bromine *Br*

Lactones from lactols – Carbohydrate derivatives
s. *2*, 293; s. a. G. R. Barker et al., Soc. *1955*, 1327

Tropolones ←

232.



A soln. of Br in CCl_4 added dropwise at 0° to 3,4,6-trimethoxycycloheptatrienecarboxylic acid in chloroform, the precipitate separated and heated 3 min. in ethyl acetate, and the resulting solid hydrolyzed with 48%-HBr at 110° for 12 hrs. → stipitatic acid. Y: 62%. R. B. Johns, A. W. Johnson, and J. Murray, Soc. *1954*, 198.

tert-Butyl hypochlorite *$(CH_3)_3C{\cdot}OCl$*

Oxidation of alcohols ←
Oxo compounds and carboxylic acid esters from alcohols
Aldehydes from α-hydroxycarboxylic acids
s. *9*, 363

Ketones from sec. alcohols CH(OH) → CO
s. *9*, 617

Oxidation-chlorination CH(OH)CH → COCCl
α-Chloroketones from alcohols
s. *9*, 618

Bromate BrO_3^-

Quinones from quinols ←
s. *7*, 341

Manganese dioxide MnO_2

Aldehydes from prim. alcohols $CH_2OH \rightarrow CHO$

233. cf. Synth. Meth. *8*, 326, 465
MnO_2 prepared by heating the carbonate or oxalate in air will oxidize representative benzyl alcohols in petroleum ether or (preferably) in ethyl ether to the aldehydes in good yield, but will not oxidize allylic alcohols appreciably. When the above MnO_2 is acid-washed and suspended in petroleum ether, it will also oxidize allylic alcohols to the aldehydes in good yield, while oxidizing satd. alcohols to a negligible extent. E. s. M. Harfenist, A. Bavley, and W. A. Lazier, J. Org. Chem. *19*, 1608 (1954).

Unsatd. oxo compounds from unsatd. alcohols $CH(OH) \rightarrow CO$
s. *8*, 326, 465; s. a. R. J. Highet and W. C. Wildman, Am. Soc. *77*, 4399 (1955); to *8*, 326 s. C. D. Robeson et al., Am. Soc. *77*, 4111 (1955); steroids with water-washed MnO_2 s. F. Sondheimer et al., Am. Soc. *77*, 4145 (1955); cis-trans isomers s. D. Y. Curtin, H. W. Johnson, Jr., and E. G. Steiner, Am. Soc. *77*, 4566 (1955)

Manganese triacetate $(CH_3COO)_3Mn$

Ketones from sec. alcohols
s. *7*, 342

Potassium permanganate $KMnO_4$

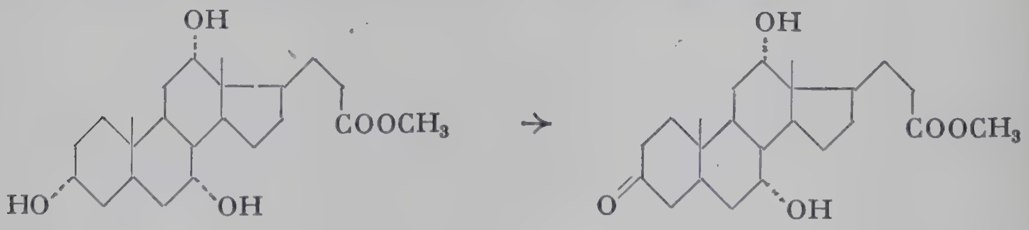
α-Ketocarboxylic acid esters
s. *7*, 343

Ketocarboxylic acids from hydroxyaldehydes ←
s. *9*, 364

Platinum/oxygen Pt/O_2

Catalytic dehydrogenation of alcohols $CH(OH) \rightarrow CO$
Preferential oxidation of steroid 3-hydroxyl groups

234.



$C_6H_5CH_2OH \rightarrow C_6H_5CHO$

O_2 passed into a soln. of methyl 3α,7α,12α-trihydroxycholanate in ethyl acetate containing Pt until absorption ceases after 16 hrs. → methyl

3-keto-7α,12α-dihydroxycholanate. Y: 70%.—Benzyl alcohol treated similarly over a period of 24 hrs. → benzaldehyde. Y: 72% as the 2,4-dinitrophenylhydrazone.—Air can be substituted for oxygen. The most satisfactory solvents are ethyl acetate, water, and dil. acetone. Acetic acid and dimethylformamide give poor yields. F. e. s. R. P. A. Sneeden and R. B. Turner, Am. Soc. 77, 190 (1955).

Via intermediates *v.i.*

Ketones from acoxy compounds via 1,1-acoxyhalides ←
1,2,3-Triketones – Labeled compounds
s. 7, 344

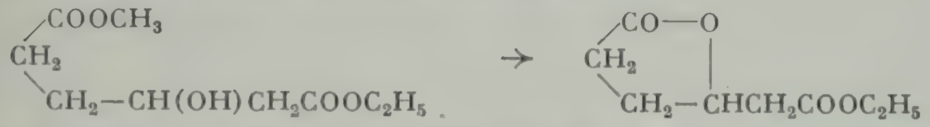
Oxygen ↑ OC ⇑ O

Without additional reagents *w.a.r.*

Lactones from hydroxycarboxylic acids ○
s. 8, 75; s. a. N. L. Drake and W. B. Tuemmler, Am. Soc. 77, 1204 (1955)

Lactones from hydroxycarboxylic acid esters

235.



Crude 1-ethyl 6-methyl d,l-3-hydroxyadipate distilled at 12 mm. Hg whereby the fore-run is returned to the flask until a constant vapor temp. of 160° is reached → d,l-5-carbethoxy-4,1-pentanolide (startg. m. f. 133). Y: 99.5%. M. Viscontini and H. Köhler, Helv. 37, 41 (1954).

Dicarboxylic acid anhydrides from dicarboxylic acids
s. 7, 345

Sodium hydroxide *NaOH*

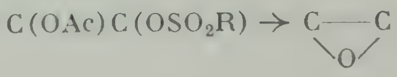
Anhydrosugars from glycosides
s. 6, 296

Potassium hydroxide *KOH*

1,1-Dilactones
s. 7, 346

Potassium hydroxide/alcohol

Oxido compounds from glycol monoesters via glycol acetate methanesulfonates



s. 9, 206

Sodium/alcohol *NaOR*

Furan ring from γ-diketones ○
s. 9, 365

Sodium carbonate *Na_2CO_3*

4-Hydroxycoumarins
s. 8, 327

Sodium acetate CH_3COONa

Lactones from hydroxycarboxylic acids with simultaneous acetylation
s. *8*, 328

Sodium acetate/acetic anhydride $CH_3COONa/(CH_3CO)_2O$

Enollactones from ketocarboxylic acids
Total synthesis of steroids
s. *8*, 329

Tert. amines/sulfonic acid chloride R_3N/RSO_2Cl
s. Sulfonic acid chloride/tert. amines

Piperidine $C_5H_{11}N$

Ketones from peroxides $CH\cdot OOR \rightarrow CO$
s. *7*, 347

Pyridine s. Acetic anhydride/-, p-Toluenesulfonyl chloride/- Thionyl chloride/- C_5H_5N

Barium hydroxide $Ba(OH)_2$

Anhydrosugars from glycosides ○
s. *7*, 348

Zinc amalgam Zn,Hg

Carboxylic acids from ketocarboxylic acids via phthalides $CO \rightarrow CH_2$
s. *9*, 366

Lithium aluminum hydride $LiAlH_4$

Isochromans ○
s. *8*, 330

O-Heterocyclics from disulfonic acid esters
s. *9*, 367

Aluminum chloride $AlCl_3$

Isocoumarins
s. *8*, 331

Acetic anhydride $(CH_3CO)_2O$

Dicarboxylic acid anhydrides from dicarboxylic acids
s. *6*, 297; *7*, 345

> **Dicarboxylic acid monoesters from dicarboxylic acids via dicarboxylic acid anhydrides**
> s. *9*, 368

Oxazolones from acylaminocarboxylic acids
s. *9*, 369; 2,2′-bis-[5(4H)-oxazolones] s. C. S. Cleaver and B. C. Pratt, Am. Soc. *77*, 1544 (1955)

3,1,4-Benzoxazones (Acylanthranils)
s. *6*, 298

Sydnones from α-N-nitrosaminocarboxylic acids
s. *10*, 37

Acetic anhydride/pyridine $(CH_3CO)_2O/C_5H_5N$

Oxazolones from acylaminocarboxylic acids
s. *7*, 349

Acetic anhydride/thionyl chloride $(CH_3CO)_2O/SOCl_2$
s. Thionyl chloride/acetic anhydride

Propionic anhydride $(CH_3CH_2CO)_2O$

Dicarboxylic acid anhydrides from dicarboxylic acids
s. *8*, 332

Trifluoroacetic anhydride $(CF_3CO)_2O$

Sydnone ring closure and opening
Mesoionic rings
s. *7*, 350

Formic acid/hydrochloric acid s. Hydrochloric acid/formic acid $HCOOH/HCl$

Oxalic acid $(COOH)_2$

Furans from γ-diketones
s. *9*, 892

Acetyl chloride CH_3COCl

Enollactones from ketocarboxylic acids
and reverse reaction
s. *7*, 351

Dicarboxylic acid anhydrides from dicarboxylic acids
s. *6*, 299; s. a. K. T. Potts and R. Robinson, Soc. *1955*, 2675

Stannous chloride $SnCl_2$

Reductive furan ring closure
s. *8*, 333

Polyphosphoric acid $H(PO_3H)_xOH$

Furan ring from γ-diketones
s. *7*, 352

Phosphorus tribromide PBr_3

N-Carboxyaminocarboxylic acid anhydrides
from N-carbalkoxyaminocarboxylic acids
s. *9*, 370

Phosphorus oxychloride $POCl_3$

Dicarboxylic acid anhydrides from dicarboxylic acids
s. *9*, 650

Phosphorus pentachloride PCl_5

2,5-Oxazolidines from N-carbalkoxy-α-aminocarboxylic acids
s. *8*, 334

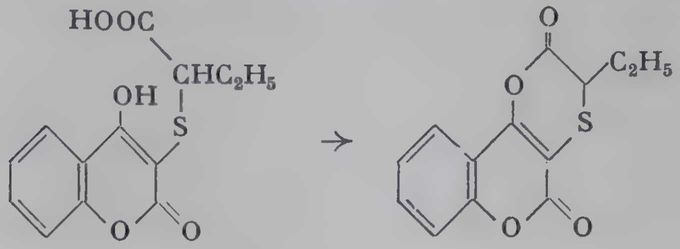
Thionyl chloride $SOCl_2$

Lactones from hydroxycarboxylic acids
s. *6*, 300

Oxazoles from acylaminoketones
s. *7*, 353

2,3-Dihydro-2,5-dioxo-5H-p-oxathiine[3,2-c][1]benzopyrans

236.



$SOCl_2$ added to a suspension of 3-(4-hydroxycoumarin)-α-thio-n-butyric acid in dry benzene, and refluxed 1 hr. → 2,3-dihydro-3-ethyl-2,5-dioxo-5H-p-oxathiino[3,2-c][1]benzopyran. Y: 76%. F.e.s. H. R. Eisenhauer and K. P. Link, Am. Soc. *76*, 1647 (1954).

Thionyl chloride/pyridine $SOCl_2/C_5H_5N$

Oxido compounds from diols
s. *8*, 335

Thionyl chloride/acetic anhydride $SOCl_2/(CH_3CO)_2O$

2,5-Oxazolidiones
from N-carbalkoxy-α-aminocarboxylic acids
s. *7*, 354

Sulfonic acid chloride/tert. amines RSO_2Cl/R_3N

Cyclic ethers from diols
s. *7*, 355

p-Toluenesulfonic acid chloride/pyridine $C_7H_7SO_2Cl/C_5H_5N$

Oxido compounds from diols
s. *8*, 335

Potassium hydrogen sulfate $KHSO_4$

Ring closure to O-heterocyclics
s. *6*, 301

p-Toluenesulfonic acid TsOH

Chromone ring from o-hydroxy-β-diketones
s. *9*, 371

p-Toluenesulfonic acid/acetic anhydride $TsOH/(CH_3CO)_2O$

Furan ring closure with subsequent deacetylation
s. *8*, 336

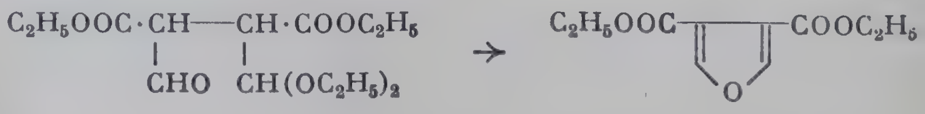
Sulfanilic acid ←

Dihydrofurans from acetylenediols
s. *7*, 356

Sulfuric acid H_2SO_4

Hetero-5-cyclic 3,4-dicarboxylic acid esters
Furan-3,4-dicarboxylic acid esters

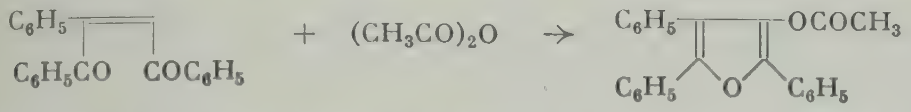
237.



General method. Furan-, thiophene-, and pyrrole-3,4-dicarboxylic acid esters can be prepared by cyclization of appropriate 1,4-dicarbonyl derivatives.—E: Diethyl 1-formyl-2-diethoxymethylsuccinate added during 5 min. at 48-52° with stirring and periodic cooling to concd. H_2SO_4, kept at 50° for an additional 5 min., cooled rapidly to 0°, and poured onto an excess of crushed ice → diethyl 3,4-furandicarboxylate. Y: 68%. F. e. s. E. C. Kornfeld and R. G. Jones, J. Org. Chem. *19*, 1671 (1954); formation of pyrones instead of furans s. Am. Soc. *77*, 4074 (1955).

Furan ring from γ-diketones

238.



A soln. of *cis*-dibenzoylstyrene in acetic anhydride containing a little concd. H_2SO_4 allowed to stand 15 min. at 0° → 3-acetoxy-2,4,5-triphenylfuran. Y: 90%.—The *cis*-isomers, although more stable, form more easily furan derivatives than the *trans*-isomers. F. e. s. R. E. Lutz and C. R. Bauer, J. Org. Chem. *19*, 324 (1954).

Dihydrofuran ring
s. *8*, 337

Dihydrofurans from acetylenediols
s. *7*, 356

Chromans
s. *9*, 372

Morpholines
s. *6*, 345

Phthalides from ketocarboxylic acids – Thiafluorans
s. *8*, 338

Pyrylium salts from diketones
s. *8*, 882

Coumarin ring
s. *8*, 339

Chromone ring from o-hydroxy-β-diketones
s. *8*, 340

Hydrochloric acid *HCl*

Cyclic ethers from diols
s. *6*, 302

Enollactones from ketocarboxylic acids
s. *8*, 341

Benzopyrans
s. *7*, 815

Isocoumarins
s. *7*, 357

Chromone ring from o-hydroxy-β-diketones
s. *8*, 342

Hydrochloric acid/formic acid *HCl/HCOOH*

Reformatskii synthesis
with subsequent Wagner-Meerwein rearrangement
Synthesis of lactones from ketones
s. *9*, 373

Hydrobromic acid *HBr*

3,4-Dihydrocoumarins
Lactones from alkoxycarboxylic acids
s. *7*, 358; 2-ketocoumarans s. H. Wolkowitz and M. S. Dunn, Biochem. Prep. *4*, 6 (1955)

Coumarin ring
Lactones from alkoxycarboxylic acid esters
Chromono(2′,3′:3,4)coumarins
s. *9*, 374

Chromone ring
s. *6*, 868

Nitrogen ↑ OC⇑N

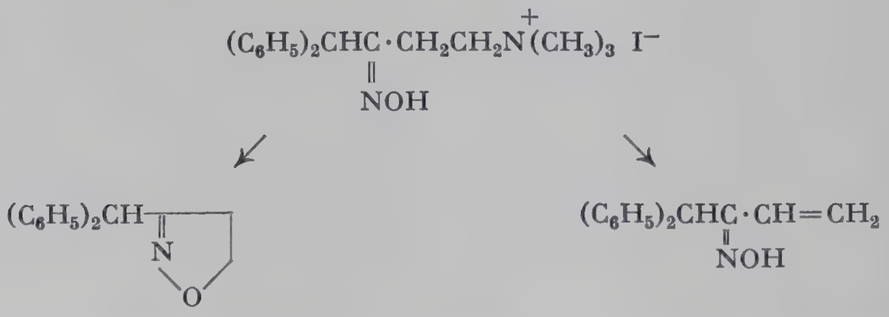
Without additional reagents *w.a.r.*

Lactones from aminocarboxylic acids ○
s. *6*, 304

Sodium hydroxide *NaOH*

Δ^2-Isoxazolines and α,β-ethyleneoximes
from quaternary β-oximinoammonium salts

239.



4-Dimethylamino-1,1-diphenylbutan-2-one oxime methiodide treated at 60-70° for 1 hr. with

NaOH in 60%-ethanol → 3-diphenylmethyl-Δ^2-isoxazoline. Y: 78%.	aq. 3%-NaOH → 1,1-diphenylbut-3-en-2-one oxime. Y: 57%.

Depending on the nature of the startg. m. and the solvent, Δ^2-isoxazolines or α,β-ethyleneoximes are formed. F. e. s. Zu-Yoong Kyi and W. Wilson, Soc. *1953*, 798.

Potassium hydroxide *KOH*

Aldehydes from 3-nitroso-2-oxazolidones C

s. 8, 922

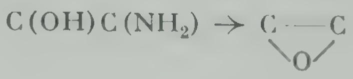
Sodium acetate *CH_3COONa*

Benzothioxol-2-ones ○

s. 9, 55

Silver oxide *Ag_2O*

Oxido compounds from aminoalcohols via quaternary ammonium salts


$C(OH)C(NH_2) \rightarrow \underset{\diagdown O \diagup}{C—C}$

s. 8, 343

Acetic anhydride *$(CH_3CO)_2O$*

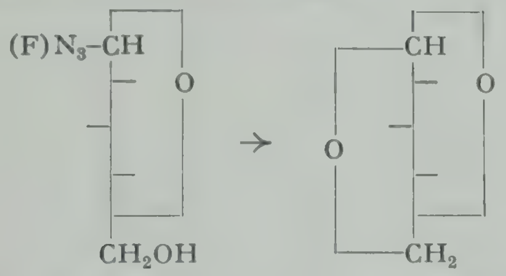
Lactones from hydroxycarboxylic acid amides ○

s. 7, 386

Amberlite ←

Glycosans from azido- und fluoro-sugars

240.



A warm aq. soln. of β-1-azido-D-glucose added to a warm aq. suspension of alkaline Amberlite IRA 400, heated 20 min. on a steam bath with stirring, then filtered →

1-Fluoro-D-glucose and alkaline Amberlite IRA 400 in water stirred 5 min. at room temp., then heated to 90° during 10 min., and filtered →

Y: 83%. levoglucosan. Y: 72%.

F. Micheel and G. Baum, B. 88, 479 (1955).

Sulfuric acid *H_2SO_4*

2-Benzoxazolones from semicarbazides

s. 7, 388

Hydrochloric acid *HCl*

Lactones from nitrocarboxylic acid esters and nitronitriles

s. 8, 344

Isoxazole ring from 1,2,3-triazine ring

s. 9, 375

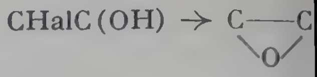
Halogen ↑ OC ⇑ Hal

Without additional reagents *w.a.r.*

Ketones from 1,1-acoxyhalides CHal(OAc) → CO

s. 7, 344

Oxido compounds from halogenhydrins


$CHalC(OH) \rightarrow \underset{O}{C—C}$

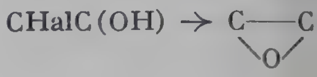
Optically active compounds s. *7*, 579

Pyrolysis of subst. 2-chloro-1-indanones ←
s. *8*, 345

Oxazolines ○
s. *8*, 346

Sodium hydroxide *NaOH*

Oxido compounds from halogenhydrins

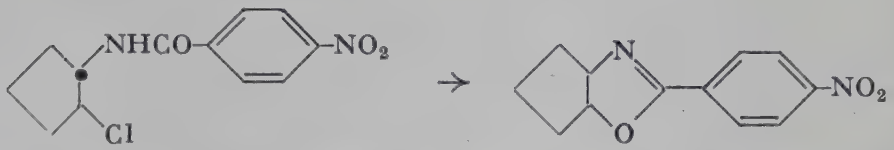

$CHalC(OH) \rightarrow \underset{O}{C—C}$

s. *6*, 305; *9*, 916; s. a. C. O. Guss and R. Rosenthal, Am. Soc. *77*, 2549 (1955)

Oxidoketones from halogenolactols ←
s. *9*, 596

Oxazolines from 2-acylaminohalides with trans-cis-rearrangement ○

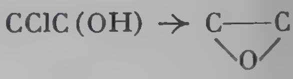
241.



A soln. of NaOH in 75%-ethanol added in one portion to a soln. of d,l-*trans*-N-p-nitrobenzoyl-2-chlorocyclopentylamine in hot 95%-ethanol, and heated ca. 1 min. on a steam bath → d,l-*cis*-2-p-nitrophenyl-4,5-trimethyleneoxazoline. Y: 86%. E. E. van Tamelen, Am. Soc. *74*, 2074 (1952).

Potassium hydroxide *KOH*

Oxido compounds from chlorohydrins


$CClC(OH) \rightarrow \underset{O}{C—C}$

s. *6*, 306

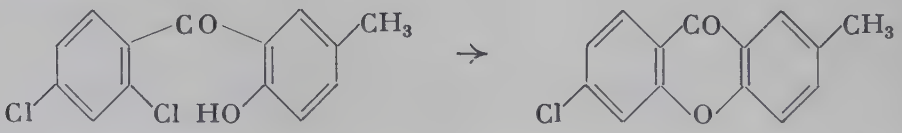
O-Heterocyclics ○

from halogenhydrins
s. *6*, 307

from acoxyhalides
s. *9*, 376

Xanthones

242.



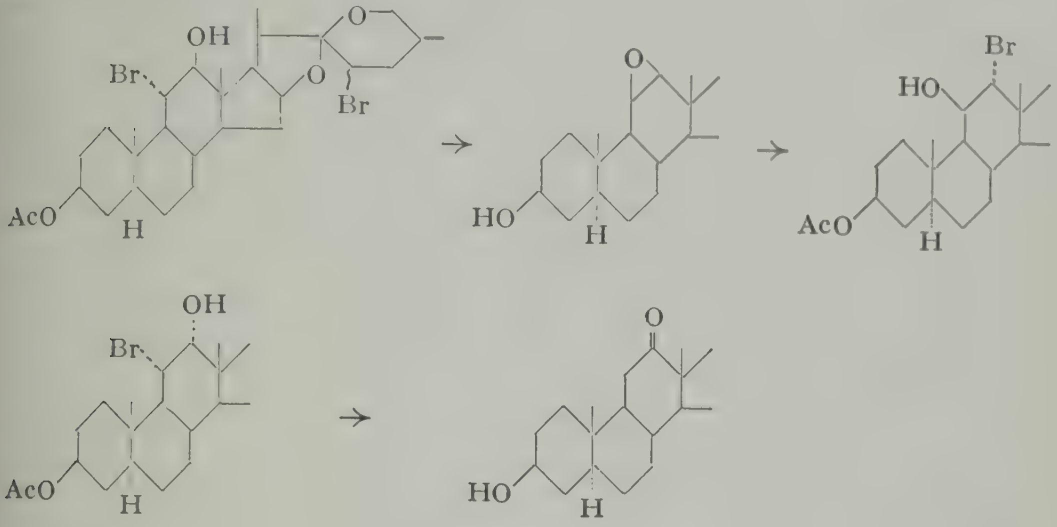
Crushed KOH added to a soln. of 2,4-dichloro-2′-hydroxy-5′-methylbenzophenone in diethylene glycol, and heated 20 min. at 50-60° with occasional shaking → 6-chloro-2-methylxanthone. Y: 83.3%. M. S. Newman and A. G. Pinkus, J. Org. Chem. *19*, 996 (1954); s. a. M. Kulka, Am. Soc. *76*, 5469 (1954).

Oxazoline ring closure and opening
s. *8*, 347

Potassium hydroxide/alcohol

Rearrangement of halogenhydrins via oxido compounds
Translocation of steroid oxygen
Ketones from halogenhydrins

243.



12β-Hydroxy- | 12α-Hydroxy-

11α,23ξ-dibromo-5α.22a-spirostan-3β-yl acetate (500 mg.) and KOH in ethanol shaken 4 hrs. at room temp. →

390 mg. 23ξ-bromo-11β,12β-epoxy-5α,22a-spirostan-3β-ol, 300 mg. treated with acetic anhydride-pyridine → 314 mg. 3β-acetate ground with acetic acid, then HBr in acetic acid added dropwise 10-15 min. with stirring, and the product isolated after a further 10 min. → 12α.23ξ-dibromo-11β-hydroxy-5α,22a-spirostan-3β-yl acetate (Y: 94%).

400 mg. 23ξ-bromo-3β-hydroxy-5α,22a-spirostan-12-one.

Translocation also with crude startg. m., a mixture of 12β- and 12α-hydroxy compounds, and without isolation of the epoxy 3β-acetate s. J. W. Cornforth, J. M. Osbond, and G. H. Phillipps, Soc. *1954*, 907.

Sodium/alcohol *NaOR*

1,4-Oxazines
α-Halogenocarboxylic acid amides
s. *6*, 308

Potassium acetate CH_3COOK

Furans
s. *6*, 309

Sodium salt Na^+

2,5-Diketomorpholines
s. *6*, 310

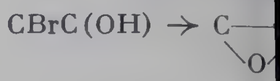
Pyridine/acetic anhydride s. Acetic anhydride/pyridine $C_5H_5N/(CH_3CO)_2O$

Copper

Phenoxathiins
s. *7*, 359

Silver oxide/pyridine Ag_2O/C_5H_5

Oxido compounds from bromohydrins
s. *9*, 60



$CBrC(OH) \rightarrow C—$

Silver acetate CH_3COO

Oxidoketones from halogenolactolides
s. *9*, 596

Barium hydroxide $Ba(OH$

Anhydrosugars from fluorosugars
s. *8*, 348

Acetic anhydride/pyridine $(CH_3CO)_2O/C_5H_5$

Pseudoxazolones
s, *7*, 360

Amberlite

Glycosans from fluorosugars
s. *10*, 240

Pyridinium ethiodide

Hydrogen chloride transfer
s. *8*, 582

Sulfur ↑ OC⇑

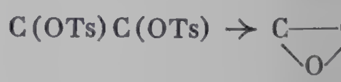
Without additional reagents *w.a.*

Oxazoline-2-thiols from bishydroxythiuram disulfides
s. *9*, 412

1,3,4-Oxadiazoles from acylthiosemicarbazides
s. *6*, 311

Potassium hydroxide *KO*

3,4-Anhydroglycitols
s. *9*, 377



$C(OTs)C(OTs) \rightarrow C—$

Sodium/alcohol *NaO*

α-Hydroxyketones from α,β-dihydroxysulfonates with rearrangement
s. *10*, 154

Calcium oxide/quinoline

Furans from sultones
s. *6*, 312

Mercuric oxide/mercuric chloride *HgO/HgC*

Thioglycosides
s. *6*, 313

Nickel *N*

γ-Lactones from γ,γ-disulfonylcarboxylic acids
s. *9*, 378

Remaining Elements ↑

OC ⇑ Rem

Without additional reagents

w.a.r.

o-Dialdehydes from cyclic selenous acid esters
s. 7, 338

C

Carbon ↑

OC ⇑ C

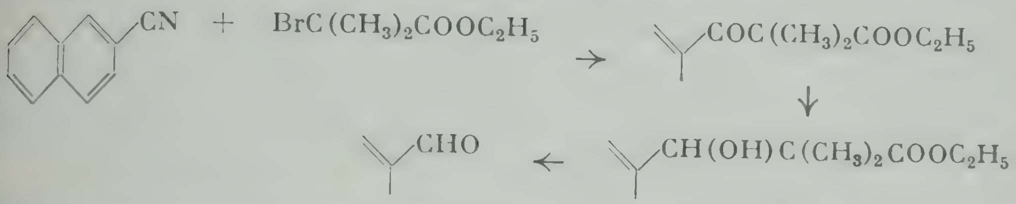
Without additional reagents

w.a.r.

Aldehydes from nitriles
via β-keto- and β-hydroxy-carboxylic acid esters

CN → CHO

244.



11.25 g. 2-cyanonaphthalene allowed to react with ethyl α-bromoisobutyrate in benzene in the presence of Zn → 13.3 g. ethyl β-naphthoyldimethylacetate hydrogenated 1 hr. with Raney-Ni in alcohol at room temp. and pressure → 12.9 g. ethyl β-(2-naphthyl)-β-hydroxy-α,α-dimethylpropionate pyrolyzed → β-naphthaldehyde. Y: 60%. F. e. s. A. Horeau and A. Ormancey, C. r. *236*, 826 (1953).

Lactones via halogenocarboxylic acid esters ○
s. 8, 349

2-Oxazolidones from N-carbalkoxy-β-halogenamines
s. 7, 361

Potassium hydroxide *KOH*

Hydrolytic cleavage of the carbon chain ←
Hydrocarbons and ketones from alcohols
s. 6, 314

Potassium hydroxide/oxygen s. Oxygen/potassium hydroxide *KOH/O₂*

Sodium/alcohol *NaOR*

Sec. alcohols from pinacols ←
s. 7, 679

Hydrolytic cleavage of the carbon chain ←
Hydrocarbons and ketones from alcohols
s. 6, 315

Furan ring from allenes ○
s. 9, 379

Potassium tert-butoxide *KOR*

Cleavage and rearrangement of ethers with bases ←
Hydrocarbons and ketones from ethers
s. 8, 350

Sodium carbonate Na_2C

Ketones from enolesters C:C(OAc) → CHC
s. *8*, 351

Silver salt/iodine Ag^+

Lactones from dicarboxylic acids
Degradation with loss of 1 C-atom
Perfluorolactones
s. *8*, 352

Acetic acid CH_3COO

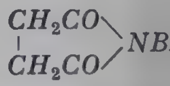
Coumaranones from o-alkoxy-α-diazoketones
s. *8*, 353

Oxalic acid (COOH)

Ketones from enolethers C:C(OR) → CHC
s. *9*, 86

Chloroform $CHCl$
s. *7*, 150

N-Bromosuccinimide



$$\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} NB$$

Oxo compounds from α-hydroxycarboxylic acids C(OH)COOH → C
s. *9*, 380

N-Bromosuccinimide and Chloramine-T ←

Aldehydes from α-aminocarboxylic acids $CH(NH_2)COOH$ → CHC
s. *8*, 354

Red lead oxide Pb_3O

Ketones from α-hydroxycarboxylic acids C(OH)COOH → C
s. *6*, 901

Phosphorus tribromide PbBr

O-Dealkylation ←
s. *8*, 355

Oxygen O

Isatin ring
s. *6*, 775

Oxygen/potassium hydroxide O_2/KO

Carboxylic acids from α-acoxyketones $COCH_2OAc$ → COO
s. *8*, 10

Hydrogen peroxide H_2O

Phenols from ar. aldehydes – Dakin reaction ←

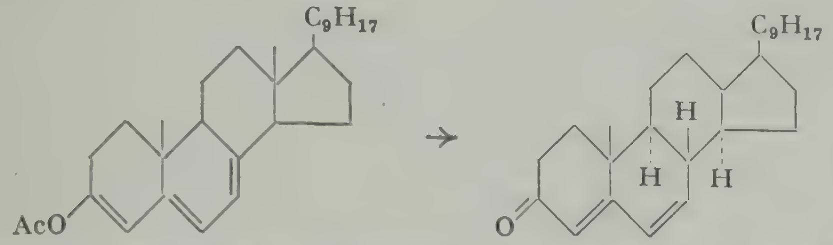
s. *4*, 283; in pyridine s. V. K. Ahluwalia, S. K. Mukerjee, and T. R. Seshadri, Soc. *1954*, 3988; also in H_2SO_4 s. A. Schönberg, N. Badran, an N. A. Starkowsky, Am. Soc. *77*, 5390 (1955)

Sulfuric acid H_2SO_4

Ketones from enolethers C:C(OR) → CHCO
s. *8*, 852; *9*, 87

Ketones from enolesters C:C(OAc) → CHCO
s. *7*, 362

245.



with migration of carbon carbon double bonds. A mixture of 3-acetoxy-ergosta-3,5,7,22-tetraene, H_2SO_4, methanol, and water refluxed ca. 3 hrs. → ergosta-4.6.22-triene-3-one. Y: 87%. A. F. Daglish, J. Green, and V. D. Poole, Soc. *1954*, 2627.

Hydrolytic cleavage of the carbon chain ←
Phenols and ketones from hydroperoxides
s. *6*, 317

Carboxylic acid esters and aldehydes from orthocarboxylic acid esters ←
s. *8*, 356

Lactones from acoxycarboxylic acid esters ○
β-Keto-γ-lactones (Tetronic acids)
s. *6*, 318

tert-Butyl hypochlorite $(CH_3)_3C{\cdot}OCl$

Aldehydes from α-hydroxycarbocylic acids CH(OH)COOH → CHO
s. *9*, 363

Sodium hypobromite $NaOBr$

Ketones from α-halogenocarboxylic acid amides $CHalCONH_2$ → CO
s. *8*, 357

Perchloric acid $HClO_4$

Hydrolytic cleavage of the carbon chain ←
Phenols and ketones from hydroperoxides
Migration aptitude
s. *6*, 319

Periodate IO_4^-

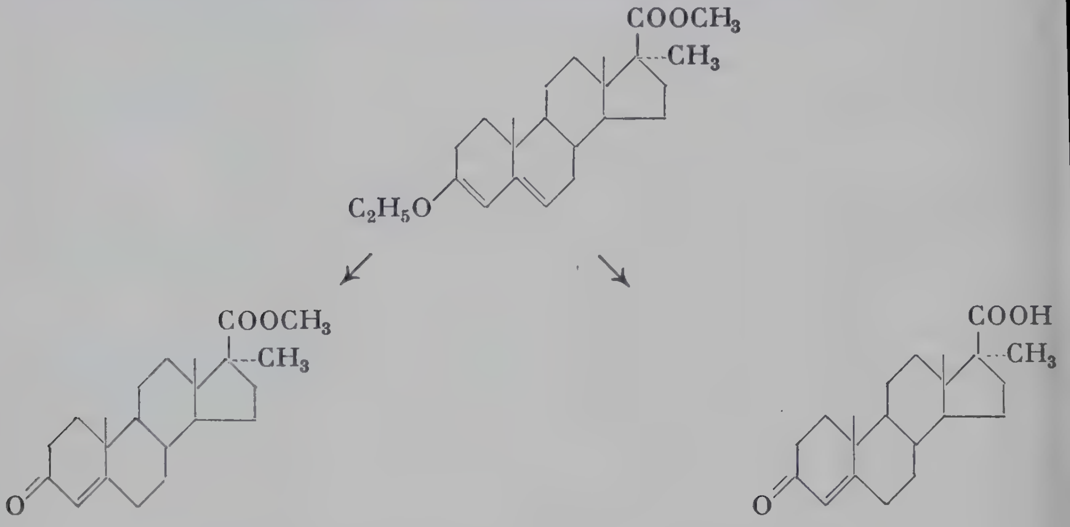
Oxidative ring opening C
s. *8*, 358

Hydrochloric acid HCl

Hydrolysis of enolethers
Enols and ketones from enolethers C:C(OR) → CHCO
s. *6*, 320

Ketones from enolethers
Carboxylic acids from carboxylic acid esters
Selective and total hydrolysis
Protection of α,β-ethylene-3-keto groups of steroids

246.



Methyl $\Delta^{3,5}$-3-ethoxy-17α-methyletiadienate

dissolved in ether-methanol, a little 2%-HCl added, and the product isolated after 24 hrs. → methyl Δ^{4}-3-keto-17α-methyletienate. Y: 83.5%.

heated 48 hrs. with methanolic KOH-soln. in a sealed tube at 168-170°, then poured into 1 *N* HCl, and extracted with chloroform → Δ^{4}-3-keto-17α-methyletienic acid. Y: 77-85%.—By formation of an enolether, the α,β-ethyleneketo group is protected against strong alkali treatment.

C. R. Engel and G. Just, Am. Soc. *76*, 4909 (1954).

Ketones from enolethers ←
s. a. *7*, 321; *8*, 716, 725; with migration of a carbon-carbon double bond s. *7*, 150

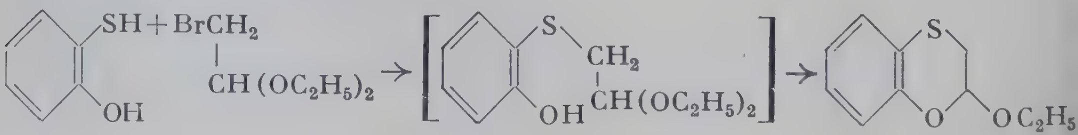
2-Pyridones from 2-alkoxypyridines ←
s. *8*, 359

Hydrolysis of isoureas ←
s. *8*, 360

Lactones from halogenocarboxylic acid esters with simultaneous replacement of carbalkoxy groups by hydrogen ←
s. *9*, 607

Benz-1,4-oxathienes from o-hydroxymercaptans ○
Thioethers from halides
Intramolecular transacetalization

247.

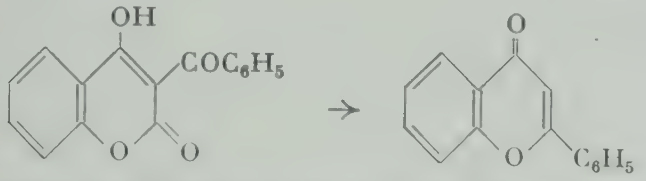


Diethyl bromoacetal added dropwise under N_2 to a well-stirred soln. of monothiocatechol and KOH in abs. ethanol, refluxed 2 hrs. under N_2, the crude product dissolved in ether satd. at 25° with HCl, and allowed to stand 24 hrs. at room temp. in a stoppered flask → 2-ethoxybenz-1.4-oxathiene (startg. m. f. 483). Y: 80.4%. W. E. Parham and J. D. Jones, Am. Soc. *76*, 1068 (1954).

1,4-Dialdehydes from 2,5-dialkoxytetrahydrofurans C
s. *9*, 381; s. a. J. Kebrle and P. Karrer, Helv. *37*, 484 (1954)

Flavones from coumarins ←

248.



A mixture of 3-benzoyl-4-hydroxycoumarin, ethanol, and concd. HCl refluxed 4 hrs. until dissolved, more HCl added, and refluxing continued for 20 hrs. → flavone. Y: 75%. F. e. in dioxane s. K. Vereš and V. Horák, Coll. Czech. Chem. Communs. *20*, 371 (1955).

Ferric sulfate/hydrogen peroxide/barium carbonate $Fe_2(SO_4)_3/BaCO_3$

Ruff degradation ←

Elimination of carbon monoxide

Degradation of glycals via aldonic acids
s. *6*, 322

Ferric sulfate/hydrogen peroxide/barium acetate $Fe_2(SO_4)_3/H_2O_2/(CH_3COO)_2Ba$

Aldehydes from α-hydroxycarboxylic acids
s. *6*, 323

Formation of N—N Bond

Rearrangement

Nitrogen/Carbon Type NN ↶ NC

Sodium nitrite $NaNO_2$

Diazo oxides from o-nitramines ○
s. *6*, 324

Exchange

Hydrogen ↑ NN ⇵ H

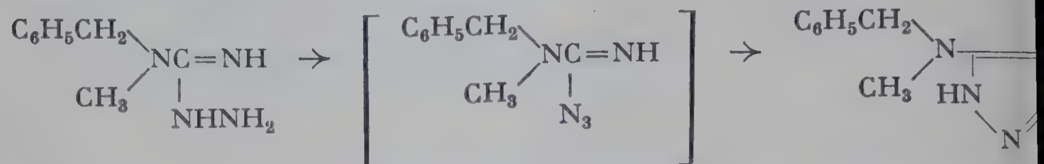
Without additional reagents *w.a.r.*

N-Nitrosamines NH → N·NO
s. *8*, 361

Sodium carbonate *Na_2C*

Tetrazole ring from aminoguanidines

249.



A soln. of 1-methyl-1-benzyl-3-aminoguanidinium nitrate, prepar
from the iodide with Ag-nitrate, in aq. HCl treated at 5-10° with a
Na-nitrite, after a starch-iodide endpoint is reached stirred for an ad
tional 15 min., Na-carbonate added portionwise whereby 1-methyl-
benzyl-2-azidoamidine precipitates which cyclizes spontaneously →
methylbenzylaminotetrazole. Y: 86.8%. F. e., also condensed tetrazo
ring, s. W. G. Finnegan, R. A. Henry, and E. Lieber, J. Org. Chem. *1*
779 (1953).

Sodium acetate *CH_3COO*

Azo compounds by coupling N:
s. *6*, 325

Sodium nitrite *NaN*

Diazo compounds from amines $CHNH_2$ → C:
s. *3*, 247; s. a. G. O. Schenck and H. Ziegler, A. *584*, 221 (1953)

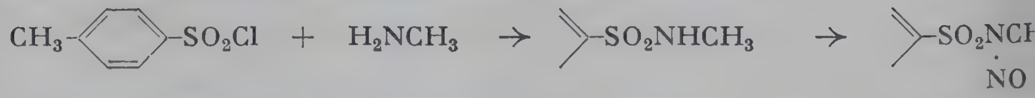
Diazonium fluoborates $\overset{+}{N_2}$ B
s. *9*, 129

N-Nitrosamines NH → N·N
s. *7*, 413

N-Nitrosoureas from ureas
s. *8*, 363

N-Nitrososulfonic acid amides from sulfonic acid chlorides via sulfonic acid amides

250.



p-Toluenesulfonyl chloride allowed to react with aq. methylamine
80-90° whereby aq. NaOH is added to neutralize the acid formed, final
heated 15 min. on a steam bath with vigorous stirring, poured in
acetic acid, cooled to ca. 5°, aq. $NaNO_2$ added dropwise during 45 mi
with stirring below 10°, and stirring continued for 15 min. → p-tol
sulfonylmethylnitrosamide (startg. m. f. 607). Y: 85-90%. T. J.
Boer and H. J. Backer, Org. Synth. *34*, 96 (1954); R. *73*, 229 (1954
f. e. s. R. *73*, 677.

Azides from amines NH_2 →
s. *8*, 363; s. a. E. Sawicki, Am. Soc. *77*, 957 (1955)

o-Azidoaldehydes from o-aminomethyl derivatives
s. *9*, 382

Diazo oxides from hydroxyamines ○
s. *7*, 268

from aminophenols
s. *9*, 383

Triazole ring
benzotriazoles s. *1*, 262-4; triazolo[d]pyrimidines s. F. F. Blicke and H. C. Godt, Jr., Am. Soc. *76*, 2798 (1954); K. L. Dille and B. E. Christensen, Am. Soc. *76*, 5087 (1954); J. Org. Chem. *20*, 171 (1955)

Tetrazolophthalazines
s. *7*, 363

Sodium nitrite/nitric acid *$NaNO_2/HNO_3$*
N-Nitrosourethans from urethans NH → N·NO
s. *9*, 384

Potassium nitrite *KNO_2*
Arbitrary formation of guanylazides or tetrazoles from aminoguanidines ←
s. *8*, 362

Sodium azide *NaN_3*
Azides from amines $NH_2 \rightarrow N_3$
s. *7*, 364

Cupric sulfate *$CuSO_4$*
1,2,3-Triazole ring via azo compounds ○
v-Triazolo[d]pyrimidines
s. *6*, 325

Sodium perborate ←
Azo compounds from amines by oxidation $2\,NH_2 \rightarrow N{:}N$
s. *7*, 365

Acetic anhydride *$(CH_3CO)_2O$*
N-Nitrosocarboxylic acid amides from carboxylic acid amides NH → N·NO

1.

$$n\text{-}C_3H_7NHCOCH_3 \rightarrow n\text{-}C_3H_7\underset{NO}{N}COCH_3$$

N-n-Propylacetamide (prepn. s. 296) dissolved in glacial acetic acid with addition of a little acetic anhydride, cooled in an ice-salt mixture, satd. with N_2O_3, then kept 12 hrs. in an ice box → N-nitroso-N-n-propylacetamide. Y: 90%. F. e. s. K. Heyns and W. v. Bebenburg, B. *86*, 278 (1953).

Nitration – N-Nitramines $N{\cdot}NO_2$
s. *6*, 326; s. a. E. H. White, Am. Soc. *77*, 6011 (1955); N-nitropyrazoles s. R. Hüttel and F. Büchele, B. *88*, 1586 (1955)

Phenyl iodosoacetate $C_6H_5I(OAc)_2$

Oxidations with phenyl iodosoacetate ←

Azo compounds from amines

Benzofurazan oxides from o-nitramines

s. *9*, 385; s. a. Soc. *1954*, 4499

Stannous chloride $SnCl_2$

Hydrazines from amines $NH_2 \rightarrow NHNH_2$

s. *9*, 569

Amyl nitrite $RONO$

Azides from amines $NH_2 \rightarrow N_3$

s. *8*, 363

Nitrosyl chloride $NOCl$

N-Nitrosation $NH \rightarrow N{\cdot}NO$

s. *6*, 327; without P_2O_5 s. Soc. *1954*, 4516

3-Nitrosooxazolidines

Hydroxyazomethine-oxazolidine isomerization

s. *9*, 386

Nitrosyl chloride/pyridine $NOCl/C_5H_5N$

N-Nitrosation

s. *8*, 364

Nitric acid HNO_3

N-Nitrosourethans from amines via urethans ←

s. *7*, 366; s. a. C. D. Gutsche and H. E. Johnson, Org. Synth. *35*, 91 (1955)

Sulfonic acid amides RSO_2NH_2

Azides from amines – Dutt-Wormall reaction $NH_2 \rightarrow N_3$

s. *7*, 367

Hydroxylamine-O-sulfonic acid NH_2OSO_3H

Hydrazines from amines $NH_2 \rightarrow NHNH_2$

s. *6*, 328

Sulfuric acid H_2SO_4

N-Nitration $NH \rightarrow N{\cdot}NO_2$

s. *8*, 365

Persulfuric acid H_2SO_5

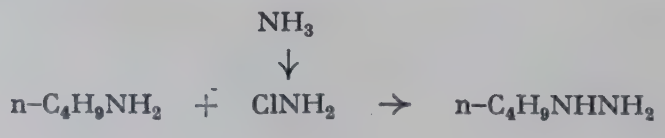
Azoxy compounds from amines $2\,ArNH_2 \rightarrow ArN(O){:}NAr$

s. *10*, 112

Sodium hypochlorite $NaOCl$

Hydrazines from amines with chloramine $NH_2 \rightarrow NHNH_2$

252.



$$n\text{-}C_4H_9NH_2 + \overset{\overset{NH_3}{\downarrow}}{ClNH_2} \rightarrow n\text{-}C_4H_9NHNH_2$$

Excess (8:1) n-butylamine added at 0° with stirring to a soln. of chloramine (from aq. NH_3 and Na-hypochlorite) containing *gelatin* to remove traces of heavy metal ions, then allowed to warm to room temp. during 2 hrs. → n-butylhydrazine. Y: 68%. F. e. s. L. F. Audrieth and L. H. Diamond, Am. Soc. *76*, 4869 (1954); *77*, 3131 (1955).

Oxygen ↑ NN⇅O

Sodium *Na*

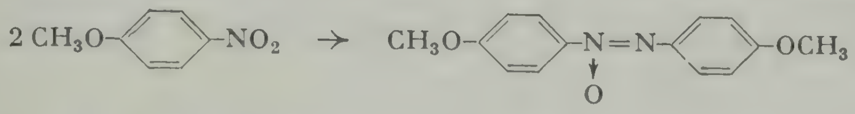
Azo compounds from nitro compounds and amines N:N

s. *8*, 366

Sodium/alcohol *NaOR*

Azoxy from nitro compounds $2\ ArNO_2 \rightarrow ArN(O):NAr$

253.



A soln. of Na in 99-100%-methanol treated with p-methoxynitrobenzene. and heated 6 hrs. on a water bath → 4,4′-azoxydianisole. Y: 95.7-97.1%. B. M. Bogoslovskiĭ, Sint. Org. *2*, 5 (1952); C. A. *48*, 621f.

Glucose ←

s. *7*, 368

Acetic acid *CH_3COOH*

Azo compounds from nitroso compounds and amines $RNO + H_2NR' \rightarrow RN:NR'$

s. *2*, 303; s. a. M. Amarosa and M. R. Cesaroni, G. *83*, 853 (1953)

Benzenesulfonyl chloride/pyridine *$C_6H_5SO_2Cl/C_5H_5N$*

Azoxy from nitroso compounds $2\ ArNO \rightarrow ArN(O):NAr$

s. *9*, 387

Via intermediates *v.i.*

Azo compounds from amines and hydroxylamines via thionylimines ←

s. *7*, 369

Sulfur ↑ NN⇅S

Without additional reagents *w.a.r.*

Azo compounds from thionylimines and hydroxylamines N:N

s. *7*, 369

Trifluoroacetic anhydride *$(CF_3CO)_2O$*

N-Nitramines from sulfonylamines $N{\cdot}SO_2R \rightarrow N{\cdot}NO_2$

s. *10*, 254

Carbon ↑ NN ⇅ C

Without additional reagents *w.a.r*

N-Nitramines – Nitrolysis N·NO

s. *7*, 370

Acetic anhydride *$(CH_3CO)_2C$*

s. *8*, 367

Trifluoroacetic anhydride *$(CF_3CO)_2O$*

N-Nitramines from acyl- and sulfonyl-amines

254.

$$\begin{tikzcd}
(n{-}C_4H_9)_2N\cdot COCH_3 \arrow[dr] & & (n{-}C_4H_9)_2N\cdot SO_2CH_3 \arrow[dl] \\
& (n{-}C_4H_9)_2N\cdot NO_2 &
\end{tikzcd}$$

N,N-Di-n-butylacetamide added dropwise at –5 to –10° to a soln. of white 98-100%-HNO_3 in trifluoroacetic anhydride, stirred 20 min. at –5°, then rapidly concentrated to half its volume by distillation at –10°/20 mm. → di-n-butylnitramine. Y: 82%.—Similarly from N,N-di-n-butylmethanesulfonamide in 87% yield.—The nitrolysis is retarded both by steric hindrance from the N-alkyl groups and by electronegative substituents. F. e. s. J. H. Robson and J. Reinhart, Am. Soc. *77*, 2453 (1955); methylene dinitramine with acetic anhydride cf. C. W. Sauer and R. P. Follet, Am. Soc. *77*, 2560 (1955).

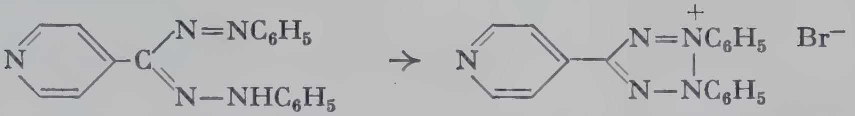
Elimination

Hydrogen ↑ NN ⇑ H

N-Halogen-amides and -imides ← ○

Tetrazolium salts from formazans
1,2,3-Triazolium salts from o-aminoazo compounds
8-Azaindazolium salts

255.



A soln. of N,N′-diphenyl-C-(4-pyridyl)formazan in ethyl acetate added portionwise with shaking to a soln. of N-bromosuccinimide in the same solvent → 2,3-diphenyl-5-(4-pyridyl)tetrazolium bromide. Y: 81%. F. e., also 1,2,3-triazolium and 8-azaindazolium salts, s. R. Kuhn and W. Münzing, B. *86*, 858 (1953); s. a. D. Jerchel and W. Edler, B. *88*, 1284 (1955).

Lead tetraacetate *$(CH_3COO)_4Pb$*

8-Azaindazolium salts

s. *7*, 371

Alkyl nitrite *RONO*

1,2,3-Triazolium salts from o-aminoazo compounds
Tetrazolium salts from formazans

s. *6*, 329

Nitric acid HNO_3

Azo from hydrazo compounds $\cdot NHNH\cdot \rightarrow \cdot N{:}N\cdot$

Azothiazoles

s. *6*, 330

Bromine *Br*

Sym. azodinitriles from sym. hydrazodinitriles

s. *6*, 869

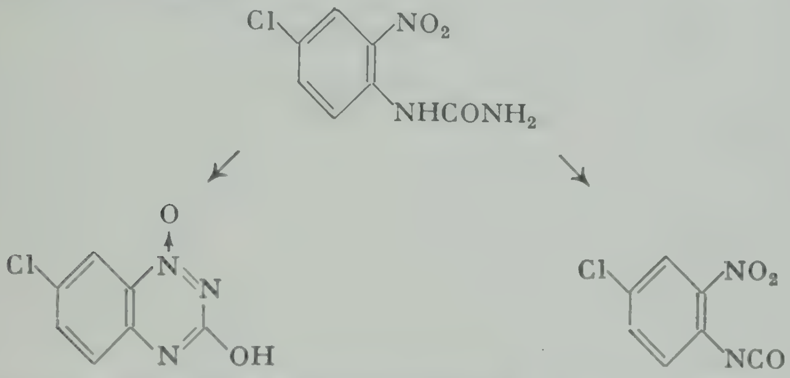
Oxygen ↑ NN ⇑ O

Sodium hydroxide *NaOH*

3-Hydroxy-1,2,4-benzotriazine 1-oxides from o-nitroureas ○

Isocyanates from ureas

256.



A suspension of 4-chloro-2-nitrophenylurea (prepn. s. 352) in

30%-NaOH heated 1.5 hr. at 90-95° with vigorous stirring → 7-chloro-3-hydroxy-1,2,4-benzotriazine 1-oxide. Y: 88%.	10%-NaOH warmed 60 hrs. on a steam bath → 4-chloro-2-nitrophenyl isocyanate. Y: 53%.

F. J. Wolf et al., Am. Soc. *76*, 4611 (1954).

Lithium aluminum hydride $LiAlH_4$

Reductive cinnoline ring closure

s. *8*, 368

Sulfur ↑ NN ⇑ S

Potassium hydroxide *KOH*

Diazo compounds from N-nitrososulfonic acid amides ←

s. *10*, 607

Carbon ↑ NN ⇑ C

Sodium hydroxide *NaOH*

Diazo compounds from amines via ureas and nitrosoureas ←

Labeled compounds s. *8*, 369

Lead tetraacetate $(CH_3COO)_4Pb$

Tetrazoles from 3,6,9-tricarbaundecaz-1,3,8,10-tetraenes ○

s. *9*, 388

Formation of N—Hal Bond

Uptake

Addition to Nitrogen

NHal ⇓ N

Without additional reagents

w.a.r.

Sec. from tert. amines
via quaternary N-halogenammonium salts
s. *7*, 542

$R_3N \rightarrow R_2NH$

Exchange

Hydrogen ↑

NHal ⇅ H

Potassium hydroxide

KOH

N-Halogenation

$NH \rightarrow NHal$

N-Halogenocarboxylic acid amides
from carboxylic acid amides
s. *7*, 559

Silver trifluoroacetate

CF_3COOAg

s. *7*, 372

Silver salt

Ag^+

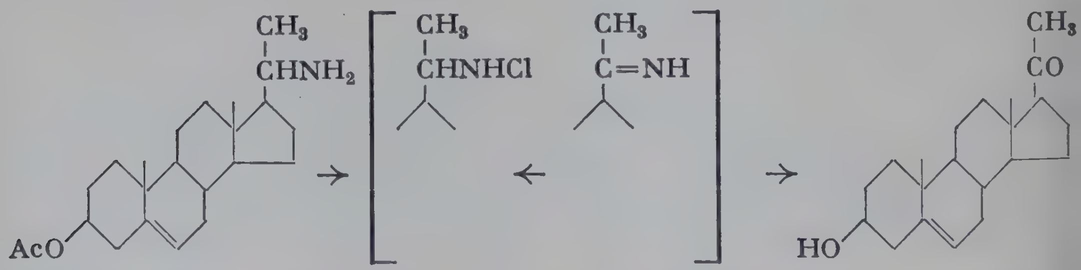
N-Iododicarboxylic acid imides
s. *9*, 389

tert-Butyl hypochlorite

$(CH_3)_3C{\cdot}OCl$

Oxo compounds from prim. amines
via N-chloramines and imines

257.



$NaHCO_3$ followed by a soln. of *tert*-butyl hypochlorite in dry ether added at 0° to a suspension of 3β-acetoxy-20-amino-5-pregnene acetate in ether, allowed to stand 20 min. in the cold, ethanol followed by a cold soln. of Na in ethanol added, heated on a steam bath without reflux and boiled until a drop of the soln. no longer gives a positive reaction with acidified starch-iodide paper, water added until the precipitated NaCl just dissolves, made strongly acid with 10%-H_2SO_4, and boiled 30 min. → 5-pregnenolone. Y: 71%.—*tert*-Butyl hypochlorite is a much more convenient reagent for the N-chlorination than is hypochlorous acid itself. F. e. s. W. E. Bachmann, M. P. Cava, and A. S. Dreiding, Am. Soc. *76*, 5554 (1954); N-chlorination with *tert*-butyl hypochlorite s. a. H. Zimmer and L. F. Audrieth, Am. Soc. *76*, 3856 (1954).

Potassium hypochlorite *KOCl*
N,N-Dichloramines from amines $NH_2 \rightarrow NCl_2$
s. *10*, 192

Formation of N—S Bond

Uptake

Addition to Oxygen and Nitrogen NS ⇓ ON

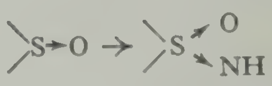
Without additional reagents *w.a.r.*
Sulfamic acids from hydroxylamines $NHOH \rightarrow NHSO_3H$
s. *9*, 390

Addition to Nitrogen and Carbon NS ⇓ NC

Sodium salt *Na^+*
Sulfonylureas from cyanamides ←
s. *7*, 373

Addition to Sulfur NS ⇓ S

Hydrazoic acid *HN_3*
Sulfoximines from sulfoxides



s. *8*, 370

Addition to Sulfur and Carbon NS ⇓ SC

Sodium hydroxide *NaOH*
Dithiocarbamic acids from amines NH → NCSSH
s. *6*, 332

Exchange

Hydrogen ↑ NS ⇅ H

Without additional reagents *w.a.r.*
1,2,5-Thiadiazole ring ○
Piazthioles (2,1,3-Benzothiadiazoles)
s. *7*, 374; s. a. F. F. Blicke and H. C. Godt, Jr., Am. Soc. *76*, 2798 (1954)

Sodium nitrite *NaNO*

Di(sulfonyl)hydroxylamines $(RSO_2)_2NOH$
s. *7*, 375

Thionyl chloride *SOCl*

Thionylimines from amines $NH_2 \rightarrow N{:}SO$
s. *7*, 369

Sulfur monochloride *S_2Cl*

Aminodisulfides from amines $2\,{>}NH \rightarrow {>}N\cdot S\cdot S\cdot N{<}$
s. *7*, 376

Iodine *I*

Thiocarbamylsulfenamides from amines via dithiocarbamic acids ←
s. *6*, 332

Sodium hypochlorite *NaOCl*

Sulfenamides from amines $NH \rightarrow NSR$
s. *6*, 331

Oxygen ↑ NS⇅O

Without additional reagents *w.a.r.*

Sulfonic acid amides from sulfonic acid anhydrides $SO_2N{<}$
s. *9*, 391

Via intermediates *v.i.*

Aminosulfonic acid amides from aminosulfonic acids ←
Protection of amino groups
s. *9*, 392

Halogen ↑ NS⇅Hal

Without additional reagents *w.a.r.*

Sulfenamides from sulfenylhalides and sulfenic acid esters ←
s. *8*, 371

Sulfamic acids $NHSO_3H$
s. *3*, 261; s. a. H. Bredereck and A. Edenhofer, B. *88*, 1306 (1955)

Sulfonic acid amides from sulfonic acid chlorides $SO_2Cl \rightarrow SO_2N{<}$
s. *9*, 392

Sulfidimides ←
s. *9*, 393

Sodium hydroxide *NaOH*

Sulfonic acid amides from sulfonic acid chlorides $SO_2Cl \rightarrow SO_2N<$
s. *10*, 250

Selective N-tosylation
s. *9*, 394

Sodium carbonate *Na_2CO_3*
s. *8*, 372

Sodium salt *Na^+*

Trichloromethylsulfenamido compounds ←
s. *8*, 373

Sulfilimines from thioethers and reverse reaction ←
s. *8*, 374

Pyridine *C_5H_5N*

Sulfenylureas from sulfenylchlorides $SCl \rightarrow SNHCONHR$
s. *9*, 395

Sulfonylaminophenols and sulfonylaminophenol sulfonic acid esters from aminophenols ←
s. *8*, 375

N-Sulfonylcyanamides from ureas ←
s. *6*, 333

Sulfur ↑ NS⇵S

Without additional reagents *w.a.r.*

N-Aminosulfides from di(thiosulfonyl)sulfides $>N\cdot S\cdot N<$
s. *8*, 376

Piperidine *$C_5H_{11}N$*

Sulfonic acid amides and sulfinic acids from disulfones ←
s. *7*, 377

Carbon ↑ NS⇵C

Without additional reagents *w.a.r.*

Sulfonic acid amides from 1,1,1-trisulfones ←
s. *7*, 378

Cleavage of sulfonylnitro compounds ←
s. *9*, 141

Sulfamic acids from isocyanates, urethans, and ureas $NHSO_3H$
s. *9*, 396

Elimination

Hydrogen ↑ **NS ⇑ H**

Iodine *I*

Tetrahydro-1,2,5-thiadiazine-6-thiones from amino-dithiocarbamic acids ○
s. *6*, 363

Sulfur ↑ **NS ⇑ S**

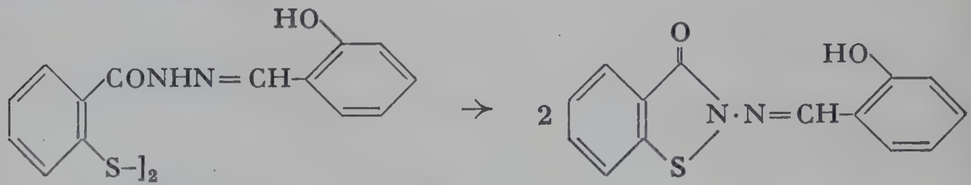
Cuprous chloride *CuCl*

1,2,3-Benzothiadiazoles from o,o′-diaminodisulfides ○
s. *6*, 334

Iodine/pyridine I/C_5H_5N

Benzisothiazolones

258.



A soln. of iodine in pyridine added to a soln. of bis-(2-hydroxybenzal)-dithiosalicylhydrazide in pyridine and the product isolated after a short time → 2-salicylalaminobenzisothiazolone. Y: 76%. F. e. and methods s. L. Katz and W. Schroeder, J. Org. Chem. *19*, 103 (1954).

Formation of N—Rem Bond

Exchange

Hydrogen ↑ **NRem ⇅ H**

Without additional reagents *w.a.r.*

Trichlorophosphazosulfonyl compounds $SO_2N:PCl_3$
s. *8*, 377; s. a. ЖК. *24*, 474 (1954); C. A. *49*, 6164a

Lithium *Li*

Aminosilanes from silanes SiH → $SiNR_2$
s. *7*, 379

Polyhalogenoalkanes ←

P-Aminophosphinic acid esters from phosphinic acid esters ←
s. *8*, 378

N-Chloramides ←

Phosphoric from phosphorous acid derivatives ←
s. *9*, 397

Oxygen ↑ — NRem ⇅ O

Without additional reagents — *w.a.r.*

Organo lead compounds ←
N-(Trialkylplumbi)sulfonamides
s. *6*, 335

Nitrogen ↑ — NRem ⇅ N

Without additional reagents — *w.a.r.*

Aminosilanes – Transamination ←
s. *7*, 380

Disilazanes — $>Si\cdot NR\cdot Si<$
s. *8*, 382

Halogen ↑ — NRem ⇅ Hal

Without additional reagents — *w.a.r.*

Diaminochlorophosphine oxides — $(R_2N)_2POCl$
s. *6*, 336

from aminodichlorophosphine oxides
s. *7*, 381

Aminodichlorophosphine oxides — $R_2N\cdot POCl_2$
s. *7*, 382

Selenylamides from selenylbromides — $SeBr \rightarrow SeN<$
s. *8*, 379

Lithium — *Li*

Aminosilanes from halogenosilanes — $SiHal \rightarrow SiN<$
Compounds with low reactivity s. *8*, 380

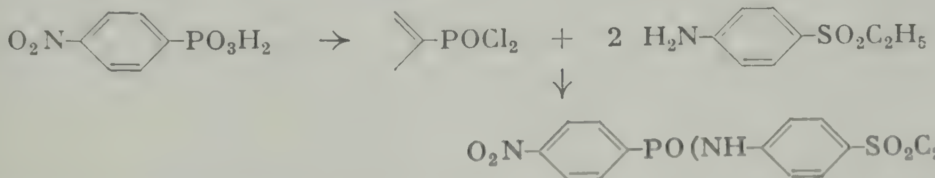
Triethylamine — $(C_2H_5)_3N$

Aminoboron dihalides — R_2NBHal_2
s. *8*, 381

Pyridine — C_5H_5N

Phosphonic acid diamides from phosphonic acids via phosphonic acid dichlorides ←

59.



p-Nitrophenylphosphonic acid intimately mixed with PCl_5, and heated towards the end of the reaction until soln. is complete → p-nitrophenylphosphonic dichloride (Y: 87-95%) dissolved in CCl_4, added to a stirred soln. of p-aminophenyl ethyl sulfone and pyridine in benzene, gently refluxed for 2.5 hrs. → N,N′-bis(p-ethylsulfonylphenyl)-P-(p-nitrophenyl)phosphonic diamide (startg. m. f. 23). Y: 77%. F. diamides, also without pyridine and without solvent, s. G. O. Doak and L. D. Freedman, Am. Soc. *76*, 1621 (1954).

Silver cyanide *AgCN*

Isocyanosilanes >SiNC
s. *9*, 398

Remaining Elements NRem⇅Rem

Without additional reagents *w.a.r.*

Aminoborans ←
s. *6*, 338

Carbon ↑ NRem⇅C

Without additional reagents *w.a.r.*

Cleavage of diarylmercury compounds ←
s. *7*, 383

Sodium amide *$NaNH_2$*

Methylaminosilanes from chloromethylsilanes ←
Disilazanes s. *8*, 382

Formation of N—C Bond

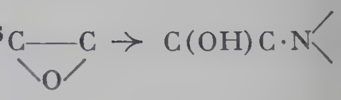
Uptake

Addition to Oxygen and Carbon NC⇓OC

Without additional reagents *w.a.r.*

N-Hydroxymethylation $N{\cdot}CH_2OH$
s. *6*, 339; *7*, 384

N-Subst. aminoalcohols from oxido compounds



$\mathrm{C{-}C(O)} \rightarrow \mathrm{C(OH)C{\cdot}N}\langle$

- **α-Hydroxy-β-aminoketones from α,β-oxidoketones**
  s. *7*, 385
- **Subst. halogenaminoalcohols from oxidohalides**
  s. *9*, 399
- **Morpholines**
  s. *6*, 345

Di(hydroxyalkyl)amines from oxido compounds ←
s. *6*, 340

α-Acylaminoalcohols from acoxyoxido compounds with simultaneous O→N acyl migration and deacetylation ←
s. *8*, 383

Oxazolidines

○

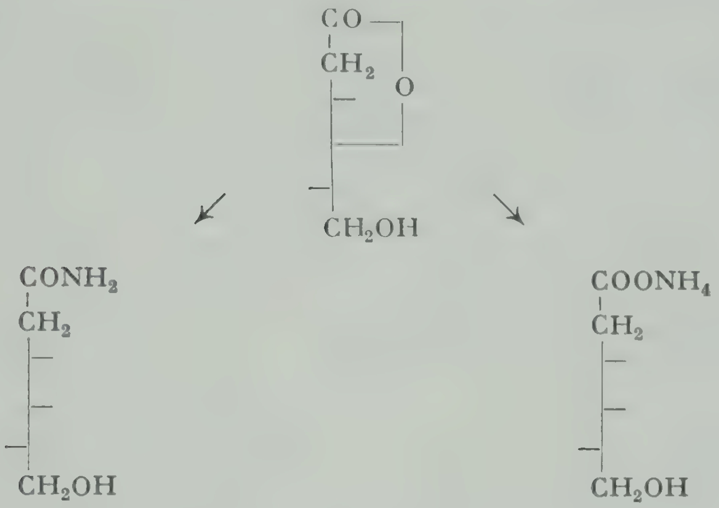
from aminoalcohols
s. *6*, 346

from cyanohydrin acetates
s. *6*, 73

Unsubst. hydroxycarboxylic acid amides and ammonium hydroxycarboxylates from lactones

C

260.



A soln. of 2-desoxy-L-galactonolactone in

liq. NH_3 allowed to stand 24 hrs. in a Dewar-flask, whereby the NH_3 slowly evaporates → 2-desoxy-L-galactonamide monohydrate. Y: 95%.

in excess dil. aq. NH_3 allowed to stand 24 hrs. at room temp. → NH_4-2-desoxy-L-galactonate. Y: 95%.

R. Grewe and H. Pachaly, B. *87*, 46 (1954).

Hydroxycarboxylic acid amides from lactones

also reverse reaction
Partial reaction of dilactones
s. *7*, 386

also aminocarboxylic acids from lactones
s. *8*, 384

Betaines from lactones

s. *8*, 385

Hydroxycarboxylic acid hydrazides from lactones

Carbohydrate derivatives s. *9*, 400

Sultone ring opening
Aminosulfonic acid inner salts from sultones

s. *6*, 343; s. a. A. *586*, 147 (1954); W. E. Truce and F. D. Hoerger, Am. Soc. *76*, 5357 (1954)

Partial dicarboxylic acid derivatives from dicarboxylic acid anhydrides

Dicarboxylic acid monoamides

s. *10*, 391; s. a. K. T. Potts and R. Robinson, Soc. *1955*, 2675; glu amines s. *6*, 342; s. a. R. W. Chambers and F. H. Carpenter, An Soc. *77*, 1522 (1955)

Acylhydrazones

s. *7*, 387

Hydroxyurethans from cyclic carbonic acid esters

s. *6*, 341; s. a. H. Najer, P. Chabrier, and R. Giudicelli, Bl. *1954*, 114

Chromone ring opening

s. *6*, 344

2,5-Oxazolidione ring opening

s. *8*, 386

Semicarbazides from 2-benzoxazolones and reverse reaction

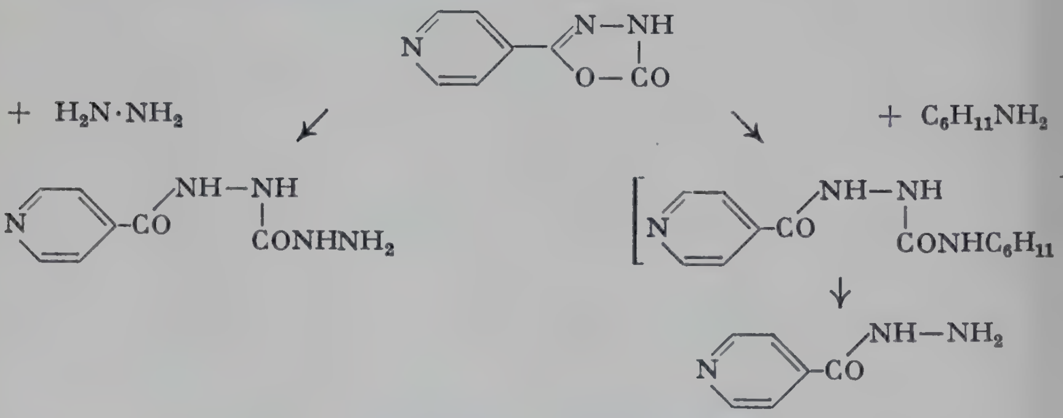
s. *7*, 388

Sydnone ring opening

s. *7*, 350

Acylcarbodihydrazides, semicarbazides, and carboxylic acid hydrazides from 1,3,4-oxadiazol-2(3H)-ones

261.



5-(4-Pyridyl)-1,3,4-oxadiazol-2(3H)-one

and hydrazine in methanol refluxed 1 hr. → 1-isonicotinylcarbodihydrazide. Y: 78%.

and cyclohexylamine refluxed 15 min → isonicotinylhydrazide. Y: almos 100%.—At lower temp., the intermediate semicarbazide can be isolated.

F. e. s. A. Stempel, J. Zelauskas, and J. A. Aeschlimann, J. Org. Chem *20*, 412 (1955).

Sodium hydroxide *NaOH*

Carboxylic acid hydroxymethylamides

CONHCH$_2$OH

s. *8*, 387

Oxazolone ring opening C
s. 5, 245; s. a. M. Brenner and K. Rüfenacht, Helv. *36*, 1832 (1953)

Sodium/alcohol *NaOR*

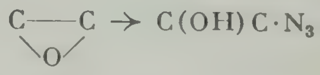
α-Aminocarboxylic acid amides
from α-aminonitriles via 5-iminoöxazolidines ←
s. *6*, 347

Sodium amide *$NaNH_2$*

Dicarboxylic acid monoamides
from dicarboxylic acid anhydrides C
s. *8*, 388

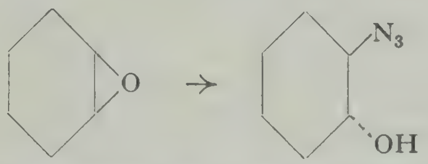
Sodium azide *NaN_3*

Hydroxyazides from oxido compounds



$$\underset{\diagdown O \diagup}{C—C} \rightarrow C(OH)C{\cdot}N_3$$

262.



Aq. NaN_3 added to a refluxing soln. of cyclohexene oxide in dioxane, refluxing continued for 20 hrs. → *trans*-2-azidocyclohexanol (startg. m. f. 27). Y: 61.4%. F. e. s. C. A. VanderWerf, R. Y. Heisler, and W. E. McEwen, Am. Soc. *76*, 1231 (1954).

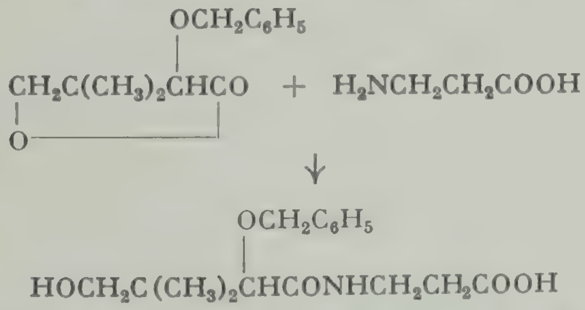
Sodium nitrite *$NaNO_2$*

Aliphatic nitrocarboxylic acids from lactones C
s. *8*, 389

Dimethylamine *$(CH_3)_2NH$*

Hydroxycarboxylic acid amides from lactones

3.

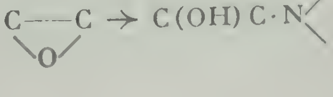


$$\underset{\llcorner O\lrcorner}{CH_2C(CH_3)_2\overset{OCH_2C_6H_5}{\overset{|}{C}}HCO} + H_2NCH_2CH_2COOH \rightarrow HOCH_2C(CH_3)_2\overset{OCH_2C_6H_5}{\overset{|}{C}}HCONHCH_2CH_2COOH$$

2.8 g. finely powdered β-alanine dissolved during 4 hrs. in a refluxing soln. of 6.95 g. pantolactone benzyl ether and dimethylamine in anhydrous methanol, and refluxing continued for 4 hrs. → 7.4 g. pantothenic acid 2′-benzyl ether (startg. m. f. 315). J. Baddiley et al., Soc. *1953*, 1610; *1954*, 2803.

Pyridine *C_5H_5N*

Aminoalcohols from oxido compounds
s. *6*, 348

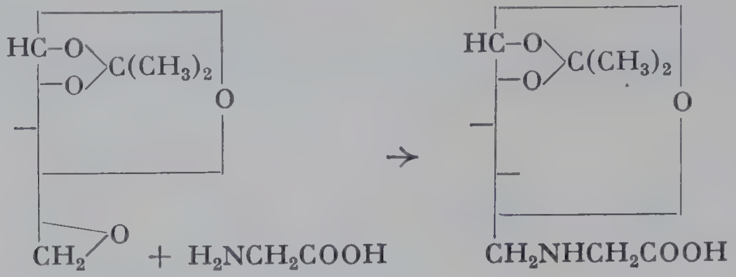


$$\underset{\diagdown O \diagup}{C—C} \rightarrow C(OH)C{\cdot}N\langle$$

Barium hydroxide *Ba(OH*

Aminosugars from anhydrosugars

264.



Glycine dissolved in 0.2 *N* $Ba(OH)_2$ on a water bath, monoaceton anhydroglucose added, and heating continued for 2.5 hrs. → 1,2-is propylidenequinovosyl-6-N-glycine. Y: 85%. F. e. s. M. Kh. Gluzma and V. I. Kovalenko, ЖК. *23,* 86 (1953); C. A. *48,* 603e.

Ethylmagnesium iodide *C_2H_5Mg*

1,1-Aminoalcohols from oxo compounds CO → C(OH)N

s. *9,* 401

Acetic acid *CH_3COO*

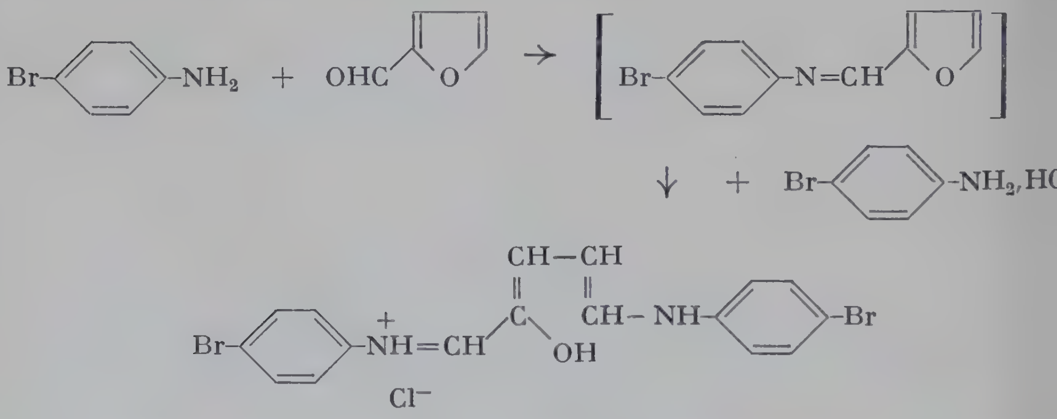
Dicarboxylic acid monoamides from dicarboxylic acid anhydrides (

s. *8,* 390; cf. T. L. Fletcher, M. E. Taylor, and A. W. Dahl, J. Org Chem. *20,* 1021 (1955)

Hydrochlorides ←

Furan ring opening – Stenhouse reaction ←

265.

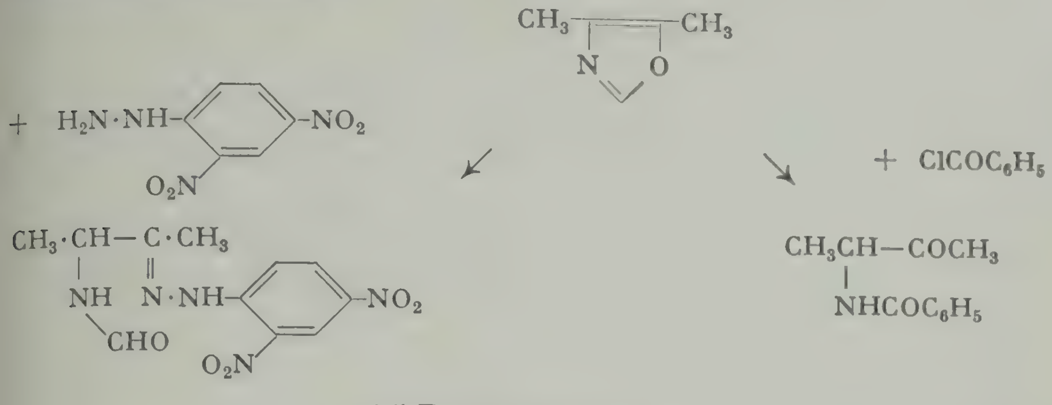


Furfural added to a soln. of p-bromoaniline in abs. alcohol, heated t 60°, allowed to cool to room temp., and a soln. of p-bromoaniline hydro chloride in abs. alcohol added with stirring → 1-p-bromophenylimino 5-p-bromophenylamino-2-hydroxypenta-2,4-diene hydrochloride. Y 86%. F. e. from the intermediate s. C. V. Brouillette, W. M. Foley, Jr and H. McKennis, Jr., Am. Soc. *76,* 4617 (1954).

Hydrochloric acid *HCl*

Oxazole ring opening

266.



4,5-Dimethyloxazole

allowed to react with 2,4-dinitrophenylhydrazine in 2 *N* HCl for 1 hr. until precipitation occurs → α-formamidoethyl methyl ketone 2,4-dinitrophenylhydrazone. Y: 71%.

dissolved in water, vigorously stirred and treated alternately with aq. 10%-NaOH and benzoyl chloride during 0.5 hr., stirring continued for 0.5 hr. → α-benzamidoethyl methyl ketone. Y: 71%.

F. e. with 2,4-dinitrophenylhydrazine s. G. Theilig, B. *86*, 96 (1953).

Ring expansion ←

N-Heterocyclics from O-heterocyclics

s. *6*, 349

Addition to Nitrogen NC⇓NN

Without additional reagents *w.a.r.*

Cyanotriazene salts from azides ←

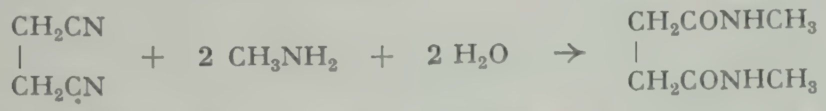
s. *7*, 389

Addition to Nitrogen and Carbon NC⇓NC

Without additional reagents *w.a.r.*

Subst. carboxylic acid amides from reactive nitriles and amines CN → CONHR

37.



$$\begin{matrix} CH_2CN \\ | \\ CH_2CN \end{matrix} + 2\ CH_3NH_2 + 2\ H_2O \rightarrow \begin{matrix} CH_2CONHCH_3 \\ | \\ CH_2CONHCH_3 \end{matrix}$$

A mixture of succinonitrile, methylamine, and water heated 8 hrs. in an autoclave at 100° → succinic acid di(methylamide). Y: 86%. F. e., with lower yields, also under atmospheric pressure, limitations, and exceptions, s. L. J. Exner, M. J. Hurwitz, and P. L. de Benneville, Am. Soc. 77, 1103 (1955).

Ureas from amines and isocyanates NH$_2$ → NHCONH
s. *8*, 391

Cyanoacetylureas
s. *8*, 408

N,N′-Disulfonylureas from sulfonylisocyanates

268. $CH_3SO_2NCO + H_2NSO_2CH_3 \rightarrow CH_3SO_2NHCONHSO_2CH_3$

A mixture of methanesulfonyl isocyanate and methanesulfonamid warmed 20 min. at 50-65° → 1,3-bis(methanesulfonyl)urea. Y: ca 100%. L. Field and P. H. Settlage, Am. Soc. *76*, 1222 (1954).

Acylureas from carbodiimides ←
s. *9*, 277

Cyanoformamidines from amines NH → NC(:NH)CN
s. *6*, 350

Isobiurets from isoureas ←
s. *6*, 351

Amidino groups from nitriles CN → C(:NH)NH
s. *8*, 392

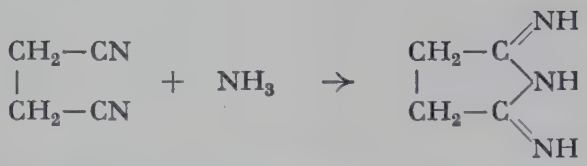
Thioureas from isothiocyanates NCS → NHC(:S)N<
s. *8*, 530, 688; s. a. F. Micheel and W. Brunkhorst, B. *88*, 481 (1955)

Thiosemicarbazides from isothiocyanates and hydrazines ←
s. *6*, 352

Acylthiosemicarbazides from acylisothiocyanates ←
s. *6*, 353

Imidines ○

269.



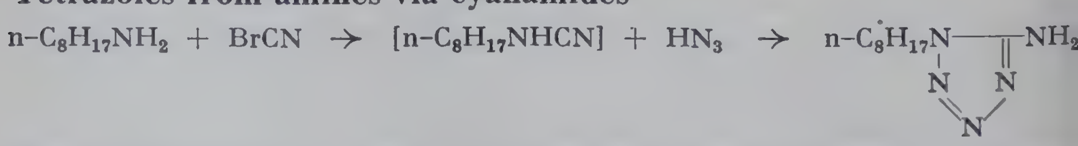
$$\begin{array}{l}CH_2-CN\\ |\\ CH_2-CN\end{array} + NH_3 \rightarrow \begin{array}{l}CH_2-C(=NH)\\ |\qquad\quad >NH\\ CH_2-C(=NH)\end{array}$$

A soln. of succinonitrile in dry methanol treated cautiously with liq. NH$_3$, then heated 18 hrs. at 70° → succinimidine (startg. m. f. 345). Y: 85%. J. A. Elvidge and R. P. Linstead, Soc. *1954*, 442; modified procedure s. Soc. *1955*, 3525.

Tetrazoles from nitriles
s. *7*, 397

Tetrazoles from amines via cyanamides

270.



$$n\text{-}C_8H_{17}NH_2 + BrCN \rightarrow [n\text{-}C_8H_{17}NHCN] + HN_3 \rightarrow n\text{-}C_8H_{17}N-NH_2$$

Cyanogen bromide in ether added dropwise with stirring and cooling to n-octylamine in ether, then an ether soln. containing ca. 0.5 mole

HN_3 added rapidly, and the resulting mixture stirred several hrs. at room temp. → 1-n-octyl-5-aminotetrazole. Y: 82%. F. e. s. W. L. Garbrecht and R. M. Herbst, J. Org. Chem. *18*, 1014 (1953).

Subst. carboxylic acid amides and carboxylic acids from carboxylic acid chlorides with subsequent lactam ring opening ↺
s. *9*, 402

Isoquinoline ring opening
s. *8*, 393

Imidazolidone ring opening
s. *7*, 390

Hydantoin ring opening
s. *9*, 436

Dianthranilide ring opening
s. *9*, 403

Oxazolidines from oxo compounds ←
s. *6*, 354

Sodium hydroxide $NaOH$

Sulfonylureas and other compounds containing the sulfonylamino group ←
s. *7*, 391

Hydantoins from α-aminocarboxylic acids via α-ureidocarboxylic acids ○
s. *9*, 404

Tert. aminoketones from hydroxy-N-heterocyclics ↺
s. *10*, 187

Imidazole ring opening
s. *6*, 355

Potassium hydroxide KOH

1,3,5-Triazines from nitriles and dicyanodiamide ○
s. *9*, 405

Potassium cyanide KCN

Quinocolls
s. *6*, 356

Potassium cyanate $KOCN$

Semicarbazides from hydrazines $NHNH_2 \rightarrow NHNHCONH_2$
s. *7*, 392; with quantitative yield s. H. Beyer, W. Lässig, and G. Ruhlig, B. *86*, 764 (1953)

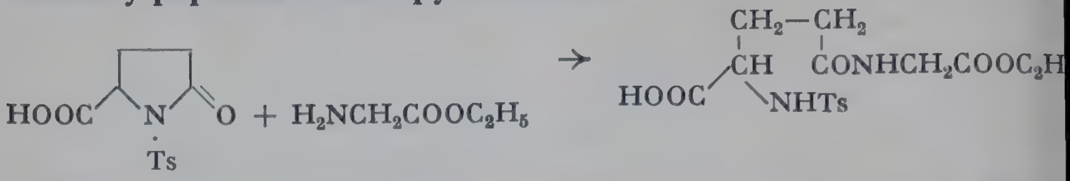
Sodium salt Na^+

Sulfonylureas from isocyanates $N{:}C{:}O \rightarrow NHCONHSO_2R$
s. *7*, 393

Triethylamine $(C_2H_5)_3N$
s. *8*, 394

N-Ethylpiperidine ←

Glutamylpeptides from 2-pyrrolidones

271. 

Anhydrous p-toluenesulfonyl-D-pyrrolidonecarboxylic acid, glycin ethyl ester hydrochloride, N-ethylpiperidine, and acetonitrile refluxe 4 hrs. → p-toluenesulfonyl-γ-D-glutamylglycine ethyl ester. Y: 80% J. Rudinger and H. Czurbová, Coll. Czech. Chem. Communs. *19*, 38 (1954); also α-glutamylpeptides s. *19*, 375.

Pyridine C_5H_5

Ureas from amines and isocyanates $NH_2 \rightarrow NHCONH$

s. *6*, 508

Calcium hydroxide *Ca(OH)*

2,5-Diketopiperazine ring opening

s. *8*, 395

Barium hydroxide *Ba(OH)*

Cyclic guanidines from diamines

s. *7*, 394

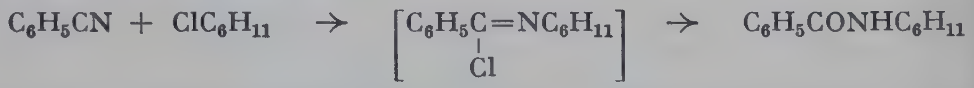
Magnesium *M*

Biguanides from cyanamides and guanidines ←

s. *6*, 357

Aluminum chloride / *AlCl*

Subst. carboxylic acid amides from nitriles and halides CN → CONH

272. 

$$C_6H_5CN + ClC_6H_{11} \rightarrow \left[\underset{Cl}{C_6H_5C}{=}NC_6H_{11}\right] \rightarrow C_6H_5CONHC_6H_{11}$$

Cyclohexyl chloride in anhydrous ether added dropwise during 3 min. to a refluxing mixture of benzonitrile and $AlCl_3$ in ether in HCl-stream, stirring and heating continued for 12 hrs., the flask stoppered, allowed to stand 12 hrs. at room temp, poured onto cracked ice and allowed to stand 6 hrs. at room temp. under a gentle flow of ai → N-cyclohexylbenzamide. Y: 47%.—HCl can be replaced by smal amounts of iodine as activating agent (Y: 46%). F. e. s. G. W. Cannon K. K. Grebber, and Yun-Kung Hsu, J. Org. Chem. *18*, 516 (1953).

Aluminum bromide *AlBr*

1,2,3-Triazines by trimerization

s. *7*, 395

Methyl alcohol CH_3O

Trimerization of nitriles to 1,3,5-triazines

s. *9*, 406

Acetic acid CH_3COOH

1-Acoxy-1-acylamines from azomethines C:N → C(OAc)NAc
s. *8*, 396

Reactions with cyanogen
Sym. bisoxamidines from amines

$RNH\underset{\underset{HN}{\|}}{C}-)_2$
s. *9*, 407

Aminoarylenedisulfonamides from quinone diimides ←
s. *8*, 397

Azidoarylenediamides from quinone diimides ←
s. *8*, 398

Sulfonylguanidines from sulfonylcyanamides ←
s. *6*, 529

Sulfonates RSO_3^-

Biguanides and subst. guanidines from cyanoguanidines ←
s. *8*, 399

Sulfuric acid H_2SO_4

Subst. carboxylic acid amides from nitriles and alcohols CN → CONHR
s. *6*, 358

1,1-Di(acylamino) compounds from nitriles ←
s. *7*, 396; s. a. M. Brenner and K. Rüfenacht, Helv. *36*, 1832 (1953)

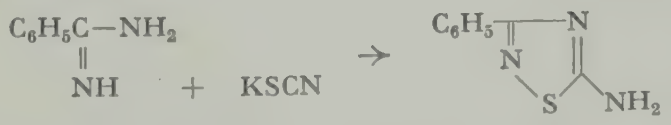
Monosubst. ureas from amines NH_2 → $NHCONH_2$
s. *8*, 400; labeled compounds s. *8*, 369

Tetrazoles from nitriles ○
s. *7*, 397

Bromine *Br*

5-Amino-1,2,4-thiadiazoles

73.



The calculated amount of Na-methoxide soln. added simultaneously with Br during 40 min. to a stirred and cooled soln. of benzamidine hydrochloride and K-thiocyanate in methanol, allowed to stand 2 hrs. in ice-water, then treated with acetic acid and satd. aq. Na-sulfide to remove excess oxydizing agent → 5-amino-3-phenyl-1,2,4-thiadiazole. Y: 75%. F. e. s. J. Goerdeler, K. Wember, and G. Worsch, B. *87*, 57 (1954).

Hydrochlorides ←

Ureas from amines NH_2 → $NHCONH_2$
s. *6*, 359

Imidazoles from α-aminoketones via 2-mercaptoimidazoles
s. *8*, 401

2-Aminothiazoles from 2-ketothiocyanates
s. *8*, 408

Hydrochloric acid

Acylsemicarbazides from carboxylic acid hydrazides
s. *9*, 409

Hydantoins from α-aminocarboxylic acids
s. *6*, 360

Addition to Halogen and Carbon NC ⇓ Ha

Without additional reagents *w.a*

Quaternary ammonium salts from betaineazeniates
s. *9*, 410

Addition to Sulfur and Carbon NC ⇓ S

Without additional reagents *w.a*

Dithiocarbamic acid esters from amines
s. *6*, 361

Tetrahydro-1,2,5-thiadiazine-6-thiones
from diamines via amino-dithiocarbamic acids
s. *6*, 363

Thiazolidine ring opening
s. *6*, 362

Thiosalicylide ring opening
Thioethers from amines
s. *9*, 411

Triethylamine $(C_2H_5)_3$

Dithiocarbamic acid esters from amines $NH_2 \rightarrow NHC(:S)S$
s. *8*, 402; *9*, 705

Pyridine C_5H_5

Thioureas from amines $NH_2 \rightarrow NHCSNH$
s. *7*, 519

Iodine

Oxazoline-2-thiols from 2-aminoalcohols
via bishydroxythiuram disulfides
s. *9*, 412

Addition to Carbon

NC⇓CC

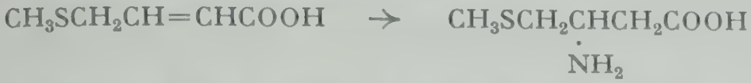
Without additional reagents

w.a.r.

β-Aminocarboxylic acids
γ-Alkylthio-β-aminocarboxylic acids
from γ-alkylthio-α,β-ethylenecarboxylic acids

$C{:}C \rightarrow CHC{\cdot}NH_2$

274.



$CH_3SCH_2CH{=}CHCOOH \rightarrow CH_3SCH_2\underset{NH_2}{CH}CH_2COOH$

γ-Methylthiocrotonic acid heated 2 hrs. with aq. NH_3 (d. 0.91) at 150-160° in a sealed tube → β-methionine. Y: 64%.—A longer reaction time lowers the yield. L. Birkofer and I. Hartwig, B. *87*, 1189 (1954); f. β-aminocarboxylic acids s. H. Feuer and W. A. Swarts, Am. Soc. *77*, 5427 (1955).

Amines from ethylene derivatives

$C{:}C \rightarrow CHC{\cdot}N<$

s. *6*, 364

α-Halogenamines from α,β-ethylenehalides
s. *8*, 403

2-Acylamino-1,1-disulfones from
1,2-ethylene-1,1-disulfones via 2-amino-1,1-disulfones

$C{:}C \rightarrow CHC{\cdot}NHAc$

s. *7*, 398

Enamines from acetylene derivatives

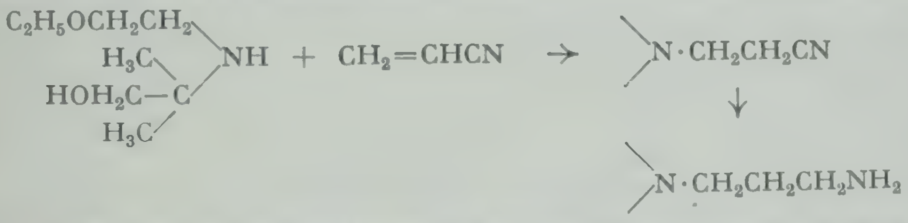
$C{\vdots}C \rightarrow CHC{:}C{\cdot}N<$

s. *7*, 217

Propylenediamines via N-cyanoethylation

$NH \rightarrow NCH_2CH_2CN$

275.



A mixture of 2-(2-ethoxyethylamino)-2-methyl-1-propanol and acrylonitrile refluxed 48 hrs. at 95-100°, the crude adduct dissolved in ether, Raney-Ni and liq. NH_3 added, then hydrogenated 3 hrs. at 100° and an initial H_2-pressure of 1350 p. s. i. → N-(2-ethoxyethyl)-N-(1-hydroxy-2-methyl-2-propyl)-1,3-propanediamine. Y: 89.5% based on unrecovered startg. m.; conversion 52%. S. M. McElvain and L. W. Bannister, Am. Soc. *76*, 1126 (1954).

1,2-Nitramines from
α,β-nitroethylene derivatives and azomethines

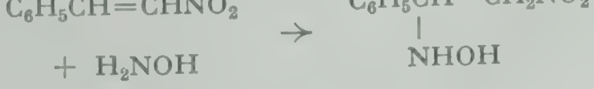
$C(NO_2)C{\cdot}N<$

s. *9*, 413

2-Nitrohydroxylamines
from 1,1-nitroethylene derivatives

$C{:}C \rightarrow CHC{\cdot}NHOH$

76.



$C_6H_5CH{=}CHNO_2 + H_2NOH \rightarrow C_6H_5\underset{NHOH}{CH}{-}CH_2NO_2$

Hydroxylamine in methanol added to a soln. of nitrostyrene in meth
nol, refluxed 30 min., then the solvent removed by a stream of air
N-(1-phenyl-2-nitroethyl)hydroxylamine (startg. m. f. 114, 369, 70
Y: 80%. F. e. s. C. D. Hurd and J. Patterson, Am. Soc. 75, 285 (195

β,γ-Ethylenehydrazines from dienes
s. *7*, 399

Carboxylic acid amides from ketenes
s. *6*, 365

Acetylation with ketene – Selective N-acetylation
s. *6*, 366

1,2,3-Triazoles from acetylene derivatives
s. *8*, 404

Sodium N

Amines from ethylene derivatives C:C → CHC·N
s. *6*, 367

Phenylethylamines
s. *6*, 368

Potassium

Pyrimidines from nitriles and acetylene
s. *9*, 414

Bases

N-Cyanoethylation of α-aminocarboxylic acids $NH \rightarrow NCH_2CH_2C$
s. *6*, 369

Sodium azide *NaN*

Azides from ethylene derivatives C:C → CHC(N
s. *9*, 415

Hydrazoic acid *HN*

Lactams from cyclic ketones – Ring expansion
s. *4*, 326; 5-homopiperazinones s. S. C. Dickerman and A. J. Besozz
J. Org. Chem. *19*, 1855 (1954)

Triton B

Phthalimides from ethylene derivatives C:C → CHC·N
s. *6*, 371; s. a. A. M. Islam and R. A. Raphael,
Soc. *1955*, 3151

Cuprous chloride *CuC*

Amines from ethylene derivatives C:C → CHC·N
s. *7*, 400

Borax Na_2B_4O

Carboxylic acid amides
from α,α-dihalogenoethylene derivatives
s. *6*, 370

Salts of org. bases

N-Cyanoethylation $NH \rightarrow NCH_2CH_2C$
β-(Arylamino)propionitriles s. *6*, 372

Ammonium acetate *CH_3COONH_4*

Pyridines from 2-cyclohexenones ←

s. 7, 401

Acetic acid *CH_3COOH*

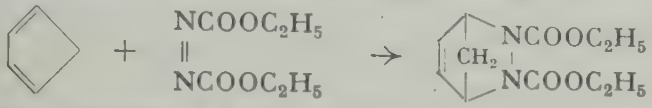
N-Cyanoethylation $NH \rightarrow NCH_2CH_2CN$

s. 8, 405

Trifluoroacetic acid *CF_3COOH*

3,6-Endomethylene-1,2,3,6-tetrahydropyridazines ←

277.

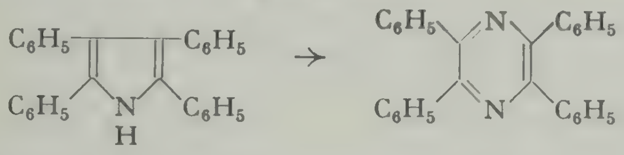


Cyclopentadiene added to a soln. of diethyl azodicarboxylate and some trifluoroacetic acid in benzene, and the product isolated after 12 min. at 5° → 1.2-dicarbethoxy-3.6-endomethylene-1,2,3,6-tetrahydropyridazine. Y: 97%. F. conditions s. A. Rodgman and G. F. Wright, J. Org. Chem. *18*, 465 (1953).

Lead tetraacetate *$(CH_3COO)_4Pb$*

Pyrazines from pyrroles – Ring expansion ←

278.



Tetraphenylpyrrole in chloroform treated with dry K-carbonate, then Pb-tetraacetate in chloroform added dropwise, finally heated some time on a water bath → tetraphenylpyrazine. Y: 40%. R. Kuhn and H. Kainer, A. *578*, 226 (1952).

Azide/chlorosulfonic acid s. Chlorosulfonic acid/azide *$N_3^-/ClSO_3H$*

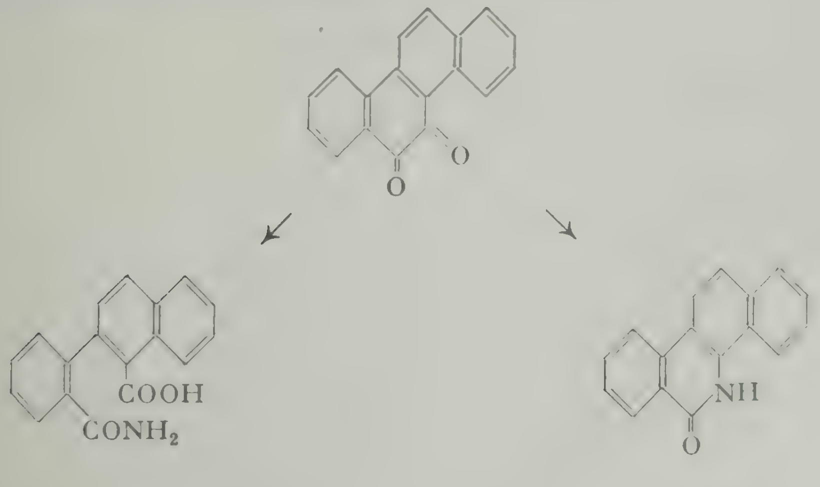
Hydrazoic acid *HN_3*

Schmidt reaction ←

Dicarboxylic acid monoamides from o-quinones

Phenanthridones from quinones

9.



A mechanically stirred soln. of chrysenequinone in concd. H_2SO_4 treated during 40 min. with 1 mole NaN_3 at such a rate that the temp. is maintained at 50°, and the product isolated after a further 30 min. at the same temp. → 2-o-benzamido-1-naphthoic acid. Y: 70%.—With excess NaN_3, 3,4-benzophenanthridone is obtained with almost 100% yield. G. M. Badger and J. H. Seidler, Soc. *1954*, 2329.

Sulfuric acid *H_2SO_4*

Amines from ethylene derivatives and nitriles via acylamines C:C → $CHC(NH_2)$

s. *9*, 416; with HCN via formamides s. Am. Soc. *77*, 5408 (1955)

2-Aminoalcohols from ethylene derivatives via pseudonitrosites C:C → $C(NH_2)C(OH)$

s. *1*, 292; improved procedure s. T. R. Govindachari and B. R. Pai, J. Org. Chem. *18*, 1253 (1953)

Chlorosulfonic acid/azide *$ClSO_3H/N_3^-$*

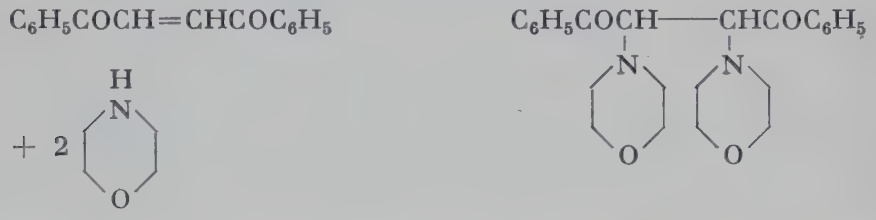
Tetrazoles from oximes – Ring expansion ←

s. *6*, 373

Iodine *I*

Reactions of iodine-amine complexes with unsatd. compounds ←
1,2-Diamines from ethylene derivatives

280.



Morpholine added to a soln. of *trans*-1,2-dibenzoylethylene in benzene, then a soln. of iodine in benzene added rapidly with stirring → crude 1,2-dimorpholino-1,2-dibenzoylethane. Y: 64%. F. e. s. P. L. Southwick and D. R. Christman, Am. Soc. *75*, 629 (1953).

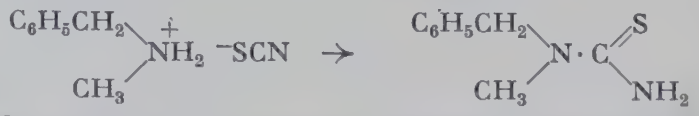
Rearrangement

Hydrogen/Nitrogen Type NC ↶ HN

Without additional reagents *w.a.r.*

Thioureas from N-subst. ammonium thiocyanates $N\cdot CSNH_2$

281.

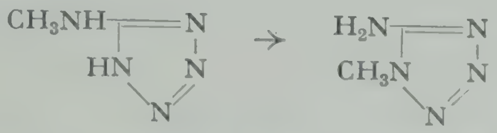


Benzylmethylammonium thiocyanate heated 3 hrs. at 150-160° → 1-methyl-1-benzylthiourea. Y: 71-76.5%. F. e. s. W. G. Finnegan, R. A. Henry, and E. Lieber, J. Org. Chem. *18*, 779 (1953).

1,2-Dihydroimidazo[1,2-a]pyrroles from α-aminomethylene compounds via α-aminopyrroles ○
s. *6*, 374

Isomerization of tetrazoles ←

82.



5-Methylaminotetrazole heated to and maintained at 180-190° for ca. 3 min. → 1-methyl-5-aminotetrazole. Y: ca. 100%. F. e. s. W. G. Finnegan, R. A. Henry, and E. Lieber, J. Org. Chem. *18*, 779 (1953).

Hydrogen/Carbon Type

NC ∩ HC

Via intermediates *v.i.*

Migration of carbalkoxyl groups ←
s. *8*, 406

Oxygen/Carbon Type

NC ∩ OC

Without additional reagents *w.a.r.*

N-Alkyl from O-alkyl OR → NR
s. *6*, 375

Alkylaminocarboxylic acids from aminocarboxylic acid esters ←
s. *7*, 402

Subst. carboxylic acid amides from iminoesters via oxazolines ←
s. *6*, 376

Quaternary cyclic N-condensed ammonium salts from sulfonic acid esters ○
s. 8, 415; s. a. B. R. Baker and J. P. Joseph, Am. Soc. *77*, 15 (1955)

Sodium hydroxide *NaOH*

Isocarbostyrils from 1-amino-1-(3-phthalidyl)alkanes via 4-hydroxy-1,2,3,4-tetrahydroisoquinolones ←
s. *8*, 407

Ureidocarboxylic acids from hydantoins C
s. *9*, 568

Potassium carbonate *K_2CO_3*

Acyl group migration OAc → NAc

as used for determination of configuration
s. *9*, 246; s. a. S. P. Findlay, Am. Soc. *76*, 2855 (1954)

Amines ←

N-Acyl from O-acyl
s. *8*, 383

n-Butylammonium carboxylate ←

1,3,5-Triazines from acyldicyanodiamides ○
s. *9*, 417

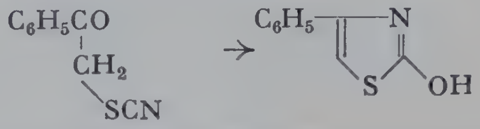
Acetic acid *CH₃COOH*

Carboxylic acid amides from carboxylic acid anhydrides ←
s. *6*, 377

Sulfuric acid and hydrochloric acid *H_2SO_4 and HCl*

2-Hydroxythiazoles from thiocyanates ○

283.

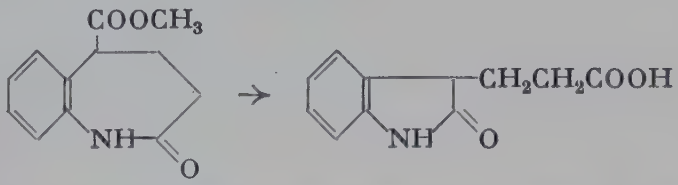


2 g. phenacyl thiocyanate added with ice-cooling to concd. H_2SO_4, and kept 40 hrs. at 0° → 1.9 g. 2-hydroxy-4-phenylthiazole. F. e. s. R. Riemschneider and G. Orlick, M. *84*, 313 (1953); with HCl s. P. L. Southwick and D. I. Sapper, J. Org. Chem. *19*, 1926 (1954).

Hydrochloric acid *HCl*

Ring contraction of N-heterocyclics ←

284.



A soln. of 2.35 g. 2-oxo-5-carbomethoxy-2,3,4,5-tetra-hydrobenzazepine in concd. HCl refluxed 3 hrs., then allowed to stand 12 hrs. at room temp. → 2.28 g. oxindole-3-propionic acid. Also with NaOH, and esters with HCl in the presence of alcohols, s. H. A. Lloyd and E. C. Horning, Am. Soc. *76*, 3651 (1954); dihydrocarbostyrils s. Am. Soc. *77*, 5932 (1955).

Nitrogen Nitrogen Type NC↶NN

Sodium/alcohol *NaOR*

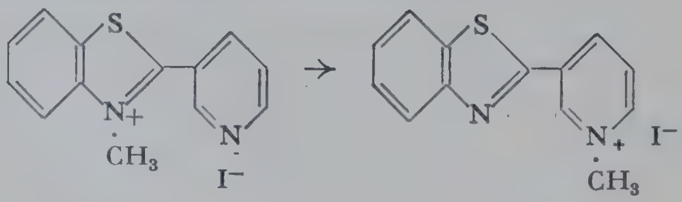
1,2,4-Triazoles from 1,4-dihydro-1,2,4,5-triazines ←
s. *7*, 503

Nitrogen/Carbon Type NC↶NC

Without additional reagents *w.a.r.*

Isomerization of quaternary ammonium salts ←

285.



1 g. 3-methyl-2-(3-pyridyl)benzothiazolium iodide heated to 225° whereby it melts at 203° → 0.96 g. (2-benzothiazolyl)-3-pyridinium methiodide. F. e. s. V. M. Zubarovskiĭ and A. I. Voronina, Ж. *23*, 140 (1953); C. A. 48, 1340i.

Sodium hydroxide *NaOH*

6-Aminouracils from cyanoacetylureas ○
s. *8*, 408

Potassium hydroxide *KOH*

2-Aminoquinoxalines via 2-amino-3,4-dihydroquinoxalines
s. *8*, 409

Sodium/alcohol *NaOR*

Pyrimidines from ureidoethylene compounds
s. *8*, 785

Sulfuric acid H_2SO_4

Phthalazones from ψ-phthalazones ←
Rowe rearrangement
s. *8*, 410

Halogen/Carbon Type NC↷HalC

Sodium hydrogen carbonate $NaHCO_3$

Piperidones from halogenaminoketones via piperidonium salts ○
s. *9*, 418

Sulfur/Carbon Type NC↷SC

Without additional reagents *w.a.r.*

Isothiocyanates from thiocyanates SCN → NCS
s. *8*, 411

Thiazolium salts from thiazolines ←
s. *6*, 378

Sodium hydroxide *NaOH*

2,4-Dithiohydantoins from thiazoles ←
s. *8*, 412

Sodium carbonate Na_2CO_3

Imidazoles from thiazoles ←
s. *6*, 379

Potassium carbonate K_2CO_3

2-Thio-1,2-dihydropyrimidines ○
s. *8*, 552

Iodine *I*

Thiazolethiones from mercaptothiazoles ←
s. *6*, 380

Carbon/Carbon Type NC↶∩C

Without additional reagents *w.a.*

Isocyanates from carboxylic acid azides $CON_3 \rightarrow N{:}C{:}$
s. *6*, 470

Hydrazones from O-azo compounds ←
s. *9*, 419

Imidazoles from isoimidazoles, also with hydrolysis ←
s. *9*, 420

2,3-Pyrrolidiones ○
s. *10*, 301

Sodium nitrite *$NaNO_2$*

1,1-Dicarbalkoxyamines $C(CONHNH_2)_2 \rightarrow C(NHCOOR)_2$
from α-dicarboxylic acid hydrazides
s. *8*, 319

2-Oxazolidones from hydroxycarboxylic acid hydrazides ○
Stereoisomers s. *7*, 403

Sulfonic acid chlorides *RSO_2Cl*

O-Carbamylhydroxamates $CONHOH \rightarrow CONHOCONHR$
from hydroxamic acids

286. $2\ C_6H_5CONHOH \rightarrow C_6H_5CONHOCONHC_6H_5$

A soln. of 4.2 g. p-toluenesulfonyl chloride in chloroform added dropwise at 10° during 15 min. to a stirred suspension of 3.2 g. Na-benzohydroxamate in chloroform, and stirring continued for 15 min. → 2.45 g. benzo(phenylcarbamylhydroxamic) acid. F. e., also with isocyanates, s. C. D. Hurd and L. Bauer, Am. Soc. *76*, 2791 (1954); in aq. soln. cf. M. A. Stolberg et al., Am. Soc. *77*, 765 (1955).

Sulfuric acid *H_2SO_4*

Alcohols from ethylene derivatives ←
and migration of a carbon-carbon double bond
via dihydrospiro-1,3-oxazines
s. *8*, 413

3-Pyrrolidones from α,β-ethylene-α′-aminoketones ○
s. *7*, 404

Hypobromite *BrO^-*

Amines from carboxylic acid amides via isocyanates ←
tert-Carbinamines – Hofmann degradation
s. *6*, 381

Thiazolo[4,5-d]pyrimidines ○
s. *8*, 414

Exchange

Hydrogen ↑ **NC⇅H**

Without additional reagents *w.a.r.*

Nitration H → NO_2

Reactions of nitrogen dioxide with ethers
s. *9*, 421

α,β-Nitroethylene derivatives
s. *10*, 182

α-Nitro-α,β-ethylenecarboxylic acid esters
s. *6*, 382

Nitration via nitronitric acid esters
s. *8*, 416

Sodium hydroxide *NaOH*

Arylazodisulfonylmethanes N:N
s. *9*, 422

Azo compounds by coupling
with simultaneous replacement of nitro by thiocyanato groups
s. *9*, 681

Potassium hydroxide *KOH*

Aliphatic-ar. azo compounds by coupling
s. *8*, 417

Sodium alkoxide/alkyl nitrite *NaOR/RONO*

Quinonemonoximes CH_2 → C:NOH
s. *7*, 405

Sodium acetate *CH_3COONa*

Aliphatic-ar. azo compounds by coupling
s. *6*, 519; *7*, 406; s. a. L. H. Smith, Jr., and P. Yates. Am. Soc. *76*, 6080 (1954)

Reaction of active methyl groups with diazonium salts ←
s. *9*, 423

Hydrazones from diazonium salts via azo compounds C
Hydrolytic ring opening
s. *7*, 406

1,1-Nitroaldehyde hydrazones from C(NO_2):NNHR
amines and aliphatic nitro compounds
s. *8*, 418; s. a. B. *88*, 1284 (1955)

ormazans from hydrazones ←
. *6*, 384

odium cyanide *NaCN*

,1-Cyanoimines from pyridinium salts C(CN):N·
6, 385

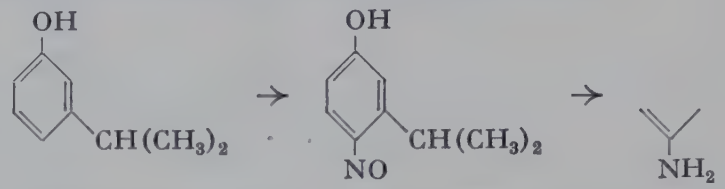
Sodium nitrite *NaNO*

Nitrosation of phenols H → N

s. *7*, 223, 407; influence of solvent s. H. Rapoport, R. H. Allen, and M E. Cisney, Am. Soc. *77*, 670 (1955)

Aminophenols from phenols via nitrosophenols

287.



Concd. HCl added to a soln. of m-isopropylphenol in 95%-ethanol, then Na-nitrite added in small portions during 2 hrs. at 5-8°, and stirring continued for 2.5 hrs. → crude 3-isopropyl-4-nitrosophenyl (Y: 89-92%) hydrogenated 45 min. with Raney-Ni in isopropanol at 55-30 p. s. i. → 3-isopropyl-4-aminophenol (Y: 87%).—Use of PtO_2 is recommended for smaller-sized runs. H. Gilman et al., J. Org. Chem. *19*, 1067 (1954); also via nitrophenols and azophenols s. H. E. Albert. Am. Soc. *76*, 4985 (1954).

2-Oximinocoumaran-3-ones from coumaran-3-ones CH_2 → C:NOH
s. *8*, 214

Azo compounds by coupling N:N
Reactions with tropolones
s. *7*, 408

Azomalondiamidines from malondiamidines
s. *7*, 469

Nitroformaldehyde hydrazones from amines $C(NO_2)$:NNHR
Diazotization
by the Erban und Mebus "nitrite paste" procedure
s. *10*, 655

Ring closures with 5-aminopyrimidines ○
1,2,4,6-Tetraazaindenes
s. *9*, 424

1,2,3-Triazine and pyrazole rings
s. *9*, 425

Sodium nitrite/sulfuric acid $NaNO_2/H_2SO_4$

Replacement of hydrogen by nitro groups ←
with migration of a carbon-carbon double bond
s. *8*, 419

Potassium nitrite KNO_2

Nitration H → NO_2
s. *9*, 426

Sodium nitrate/hydrofluoric acid $NaNO_3/HF$
s. Hydrofluoric acid/sodium nitrate

Potassium nitrate KNO_3

Nitramines
s. *8*, 420

Labeled compounds
s. *9*, 427

Pyridine C_5H_5N

s. *7*, 409

Formazans from hydrazones ←
s. *8*, 421

Pyridine/oxygen s. Oxygen/pyridine C_5H_5N/O_2

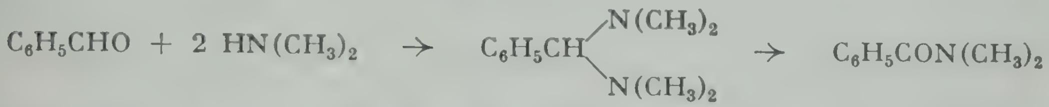
Cupric nitrate $Cu(NO_3)_2$

Menke nitration $H \rightarrow NO_2$
s. *6*, 386; *9*, 428

2-Nitropropane $(CH_3)_2CH{\cdot}NO_2$

Subst. carboxylic acid amides from aldehydes via 1,1-diamines $CHO \rightarrow CON\langle$

88.



$$C_6H_5CHO + 2\ HN(CH_3)_2 \rightarrow C_6H_5CH\begin{matrix} N(CH_3)_2 \\ N(CH_3)_2 \end{matrix} \rightarrow C_6H_5CON(CH_3)_2$$

Benzaldehyde poured into aq. 25%-dimethylamine, and heated 10 min. on a steam cone with occasional swirling → benzylidenebisdimethylamine (Y: 80%) heated at 120-130° in an oil bath, treated dropwise during 2.5 hrs. with 2-nitropropane, heating continued 1 hr., then distilled → N,N-dimethylbenzamide (Y: 94%). F. e. of the second step s. S. V. Lieberman, Am. Soc. **77**, 1114 (1955).

Acetic anhydride $(CH_3CO)_2O$

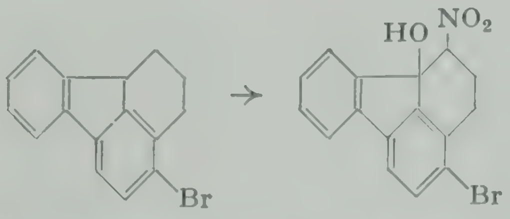
Nitration
s. *8*, 422

Acetic acid CH_3COOH

5-Nitropyrimidines
s. *7*, 410

2-Nitroalcohols from hydrocarbons ←

9.

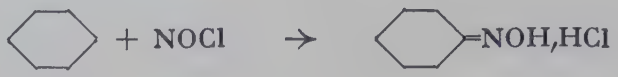


Fuming HNO_3 added dropwise at 80° to a soln. of 11.5 g. 5-bromo-1,2,3,4-tetrahydrofluoranthene in glacial acetic acid, and the product isolated after 1 hr. → 4.88 g. 5-bromo-1,2,3,4-tetrahydro-1-hydroxy-2-nitrofluoranthene. F. e. s. N. Campbell and J. F. K. Wilshire, Soc. *1954*, 867.

Alkyl nitrite/sodium alkoxide $RONO/NaOR$
s. Sodium alkoxide/alkyl nitrite

Nitrosyl chloride/irradiation ←
Oximes from hydrocarbons $CH_2 \rightarrow C{:}NOH$

290.



NOCl swept by dry N_2 at -25° onto an irradiated mixture of cyclohexane and benzene over a period of 5 hrs. → cyclohexanone oxime hydrochloride. Y: > 71%. M. A. Naylor and A. W. Anderson, J. Org. Chem. *18*, 115 (1953).

Alkyl nitrate/sulfuric acid $RONO_2/H_2SO_4$
Mononitration $H \rightarrow NO_2$
s. *8*, 423

Acetyl nitrate CH_3COONO_2
Nitration
s. *8*, 424

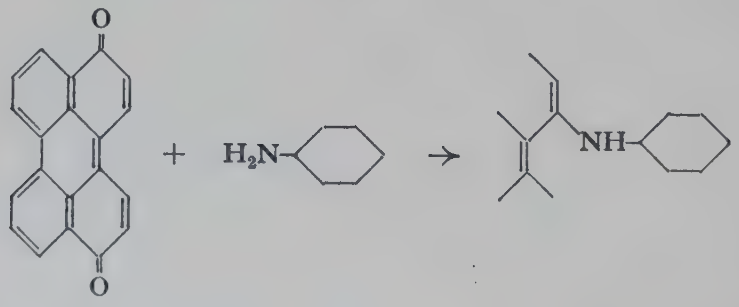
Nitrates/oxygen ←
Amination H → N<
s. *9*, 429

Phosphoric acid H_3PO_4
Nitration $H \rightarrow NO_2$
s. *10*, 135

Vanadium pentoxide V_2O_5
Replacement of hydrogen by amino groups $H \rightarrow NH_2$
s. *6*, 387

Oxygen/pyridine O_2/C_5H_5N
Amination of extended quinones H → N<

291.



200 mg. perylene-3,10-quinone heated 24 hrs. at 80° with a large excess of cyclohexylamine and pyridine in the presence of air → 217 mg. 1-cyclohexylaminoperylene-3,10-quinone. F. e. s. B. R. Brown and A. R. Todd, Soc. *1954*, 1280.

Sulfamic acid *HSO_3NH_2*

Azo compounds by coupling N:N

s. *8*, 425

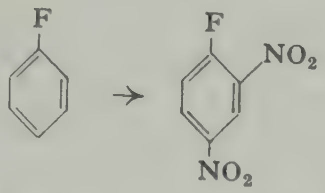
Sulfuric acid *H_2SO_4*

Nitrosation H → NO

s. *7*, 223

Nitration H → NO_2

292.



Fluorobenzene added at 70-75° with efficient stirring to a mixture of concd. H_2SO_4 (d. 1.83) and concd. HNO_3 (d. 1.42), the temp. raised to 85° over a period of 10 min., and kept 30 min. at this temp. → 2,4-dinitrofluorobenzene. Y: 82%. G. C. Finger and J. L. Finnerty, Biochem. Prep. *3*, 120 (1953).

s. a. *6*, 593; *7*, 478; K. A. Kobe et al., Ind. Eng. Chem. *46*, 728 (1954); *47*, 785 (1955); continuous process s. F. Meissner, G. Wannschaff, and D. F. Othmer, Ind. Eng. Chem. *46*, 718 (1954)

Replacement of hydrogen by amino groups via nitro compounds
N-Oxides as intermediates

s. *6*, 389

Azo compounds by coupling N:N
Disazo compounds with different components
Influence of substituents

s. *7*, 411

Molybdenum trioxide-alumina *MoO_3-Al_2O_3*

Nitriles from Hydrocarbons CH_3 → CN

s. *6*, 388

Iodine *I*

Quaternary ammonium salts from ketones ←
King reaction

Pyridinium salts s. *8*, 300

Hydrofluoric acid/sodium nitrate *$HF/NaNO_3$*

Nitration – Fredenhagen process H → NO_2

s. *7*, 412

Hydrochloric acid *HCl*

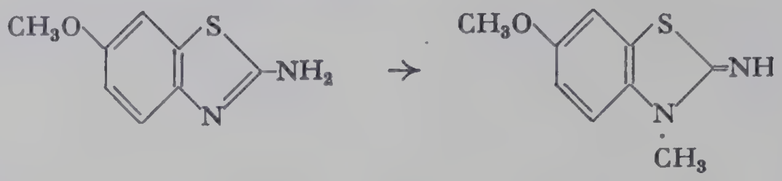
α-Isonitrosoketones from ketones $COCH_2$ → COC:NOH

s. *6*, 390

Via intermediates *v.i.*

3-Subst. 2-iminobenzothiazolines from 2-aminobenzothiazoles ←

293.



A mixture of 2-amino-6-methoxybenzothiazole and methyl p-toluenesulfonate heated over a free flame until molten, heating continued 20 min. at 140-150°, dissolved in water, and treated with aq. KOH → 2-imino-6-methoxy-3-methylbenzothiazoline (startg. m. f. 605). Y: 77%. G. M. Oksengendler, Ж. *23*, 135 (1953); C. A. *48*, 672e.

Nitration via N-nitrosamines H → NO_2
s. *7*, 413

9-Nitroanthracenes from anthracenes via 9-nitro-10-chloro-9,10-dihydroanthracenes
s. *7*, 414

Oxygen ▲ NC⇅O

Without additional reagents *w.a.r.*

Nitramines from nitroalcohols OH → N<
s. *6*, 391

α-Aminonitriles from cyanohydrins
s. *6*, 392; s. a. C. B. Pollard and L. J. Hughes, Am. Soc. *77*, 40 (1955)

Prim. amines from ethers OR → NH_2
s. *6*, 393

Sec. and tert. amines from sulfonic acid esters OSO_2R → N<
s. *7*, 415

Amines from tosylates OTs → N<
s. *6*, 394

Quaternary ammonium salts from sulfonic acid esters
Carbohydrate derivatives s. *9*, 430

Glycosamines OH → NHR
s. *7*, 416; *8*, 85

and their hydrolysis
s. *7*, 417

α-Nitro-acylamines from α-nitro-acoxy compounds OAc → NHAc
s. *7*, 418

Aminomethyl sulfones from sulfinic acids via hydroxymethyl sulfones SO_2CH_2NHR
s. *8*, 426

Aminomethylene from hydroxymethylene compounds $C{:}C{\cdot}OH \rightarrow C{:}C{\cdot}N\langle$
s. *7*, 419

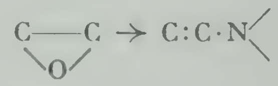
Prim. aminomethylene from alkoxymethylene compounds $C{:}C{\cdot}OR \rightarrow C{:}C{\cdot}NH_2$
s. *8*, 427

Aminomethylene from alkoxymethylene compounds $C{:}C{\cdot}OR \rightarrow C{:}C{\cdot}N\langle$
s. *6*, 397; s. a. Soc. *1955*, 1834; E. B. Knott, Soc. *1954*, 1482

Prim. enamines from ketones $CHCO \rightarrow C{:}C{\cdot}NH_2$
s. *6*, 395

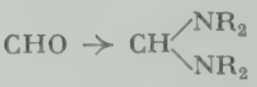
Protection of steroid 3-keto groups by formation of enamines
Sec. alcohols from ketones $C{:}C{\cdot}N\langle$
s. *8*, 428; s. a. Am. Soc. *75*, 5927 (1953)

Enamines from oxido compounds
s. *7*, 420



Enamines as intermediates in the quinoline ring synthesis $C{:}C{\cdot}N\langle$
s. *6*, 396

1,1-Diamines from aldehydes
s. *10*, 288



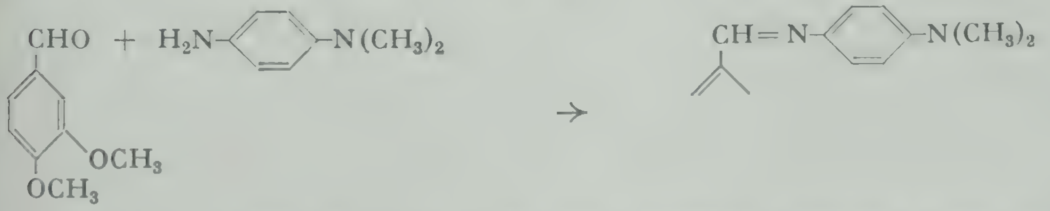
$$CHO \rightarrow CH\begin{matrix}NR_2\\NR_2\end{matrix}$$

Azomethines from amines and oxo compounds $NH_2+OC \rightarrow N{:}C$
s. *6*, 741; *7*, 421; *10*, 677

by azeotropic distillation
s. 8, 550; from weakly basic ar. amines s. B. A. Poraĭ-Koshits and A. L. Remizov, Ж. *24*, 372 (1954); C. A. *49*, 4572h

p-Dimethylaminoanils as derivatives of aldehydes
Separation of aldehydes from ketones

1.



An alc. soln. of N.N-dimethyl-p-phenylenediamine prepared from p-nitrosodimethylaniline, Zn-dust, and a little NH_4Cl added to a soln. of veratraldehyde in acetone → veratraldehyde p-dimethylaminoanil. Y: 85%.—Acetone does not react with the reagent. F. e. s. G. E. Utzinger and F. A. Regenass, Helv. *37*, 1901 (1954).

Nitrones from hydroxylamines NHOH → N(O):C
s. *8*, 429

Hydrazino- from alkoxy-tropolones OR → $NHNH_2$
s. *8*, 430

Hydrazones CO → C:NNHR
s. *9*, 121

Resolution of racemic oxo compounds via acylhydrazones C:NNHAc
s. *9*, 431

Sulfonylhydrazones $CH{:}NNHSO_2R$
Characterization of carbohydrates
s. *8*, 431

Semicarbazones CO → $C{:}NNHCONH_2$
s. *8*, 432

Thiosemicarbazones, also by interchange CO → $C{:}NNHCSNH_2$
s. *8*, 432

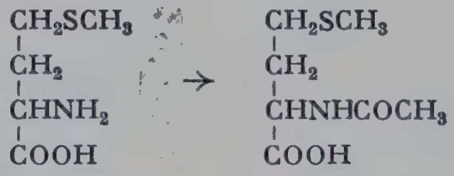
Thiocarbazones from aldehydes ←
s. *8*, 433

Dithiocarbalkoxyhydrazones CO → C:NNCSSR
s. *9*, 433

Formamides NHCHO
s. *8*, 434; *9*, 113

Acylation of amines NH → NAc

295.

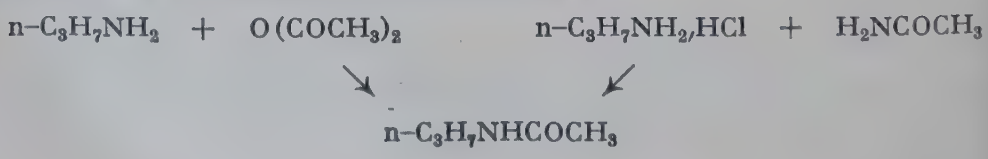


$$CH_2SCH_3{-}CH_2{-}CHNH_2{-}COOH \rightarrow CH_2SCH_3{-}CH_2{-}CHNHCOCH_3{-}COOH$$

DL-Methionine kept with acetic anhydride in acetic acid at room temp. for 3 hrs. → N-acetyl-DL-methionine. Y: 80-85%. G. P. Wheeler and A. W. Ingersoll, Am. Soc. *73*, 4604 (1951); acetylation at reflux temp. s. H. Stetter and E.-E. Roos, B. *87*, 566 (1954); trifluoroacetylation in benzene s. T. L. Fletcher, M. E. Taylor, and A. W. Dahl, J. Org. Chem. *20*, 1021 (1955).
s. a. *9*, 392

Acylation of amines
Substitution of carboxylic acid amides

296.



$$n{-}C_3H_7NH_2 + O(COCH_3)_2 \rightarrow n{-}C_3H_7NHCOCH_3 \leftarrow n{-}C_3H_7NH_2{,}HCl + H_2NCOCH_3$$

Acetic acid added slowly to n-propylamine, then acetic anhydride added, refluxed 30 min., and fractionally distilled

A mixture of n-propylamine hydrochloride and acetamide heated until molten, heating continued for several min.

Y: 88-90%. N-n-propylacetamide (startg. m. f. 251). Y: 70%.

F. e. s. K. Heyns and W. v. Bebenburg, B. *86*, 278 (1953).

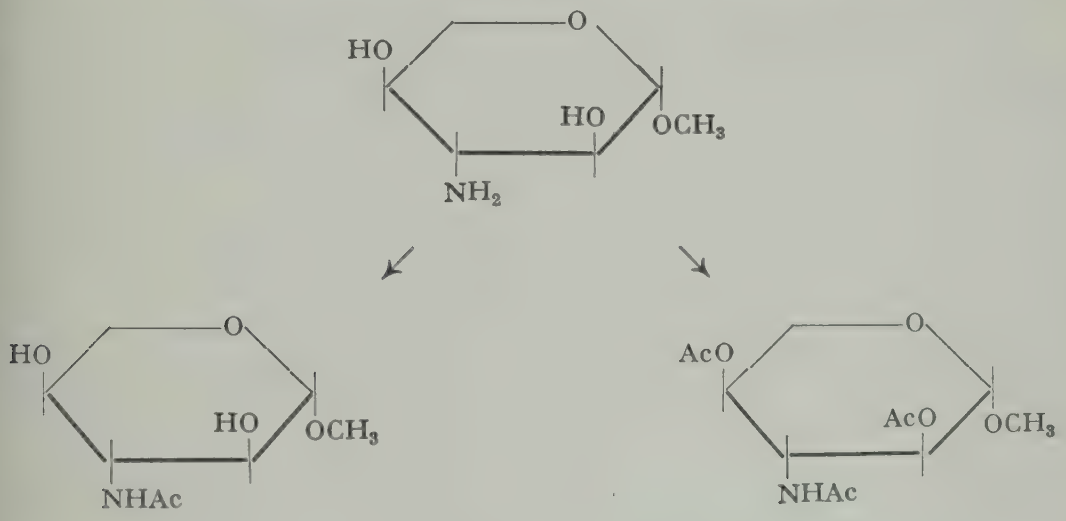
Reaction of isopropenyl acetate
N-Acetylation
s. *6*, 208; s. a. J. H. Boyer, Biochem. Prep. *4*, 54 (1955)

Partial N-acylation
s. *7*, 422

Selective N-acylation
Acylaminoalcohols from aminoalcohols
s. *7*, 423

Selective N-acetylation and total acetylation of aminoglycosides

297.



Acetic anhydride added

to an aq. soln. of methyl 3-amino-β-L-xylopyranoside, and shaken for 5 min. → methyl 3-acetamino-β-L-xylopyranoside. Y: 97%. Also in 50%-acetic acid

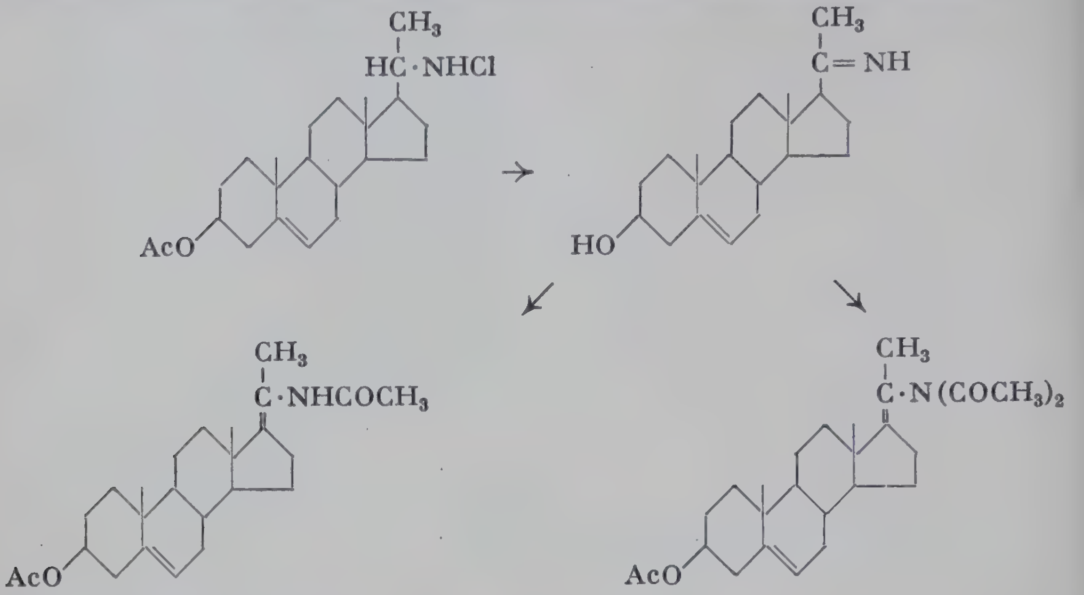
portionwise with ice-cooling to a mixture of methyl 3-amino-β-L-xylopyranoside and pyridine at a rate to keep the temp. at 20-25°, and allowed to stand 20 hrs. at room temp. in a stoppered flask → methyl 3-amino-β-L-xylopyranoside triacetate. Y: 95-98%

and f. e. s. B. R. Baker and R. E. Schaub, J. Org. Chem. *19*, 646 (1954).

1,1-Di(acylamino) compounds C(NHAc)$_2$
s. *7*, 424

Enacet- and enediacet-amines from N-chloramines via imines ←

298.



20-Chloramino-3β-acetoxy-5-pregnene added with stirring to a cold soln. of Na in abs. methanol, heated slowly to boiling, refluxed gently for 40-50 min., evaporated to dryness in vacuo under anhydrous conditions in a N_2 atmosphere, acetic anhydride

and glacial acetic acid (2:1) added portionwise with cooling, and gently refluxed on a steam bath for 1 hr. after the exothermic reaction has subsided → 20-acetamino-3β-acetoxy-5,17(20)-pregnadiene (startg. m. f. 175). Y: 75%.

added with ice-cooling, ethyl acetate and acetic acid distilled off when the exothermic reaction has subsided until a vapor temp. of 134° is reached, more acetic anhydride added, and vigorously refluxed for 65 min. → 20-diacetamino-3β-acetoxy-5,17(20)-pregnadiene. Y: 84%. —The semicyclic double bond is hindered and does not react with perbenzoic acid (cf. 175) or bromine.

Also isolation of the intermediate s. H. Ruschig et al., B. *88*, 883 (1955).

(Diacylamino)carboxylic acids
from acylaminocarboxylic acids NHAc → N(Ac)$_2$
Protection of carboxyl groups by formation of benzyl esters
s. *9*, 434

Subst. carboxylic acid amides
from carboxylic acids COOH → CONHR
s. *8*, 435

Unsubst. carboxylic acid amides
from carboxylic acid esters COOR → CONH$_2$

s. *1*, 306/7; *2*, 359; s. a. C. A. Grob and E. Renk, Helv. *37*, 1672 (1954); separation of isomers s. G. O. Schenck and H. Ziegler, A. *584*, 221 (1953)

Carboxylic acid amides from carboxylic acid esters

COOR → CON<

β-Ketocarboxylic acid amides

s. *8*, 436

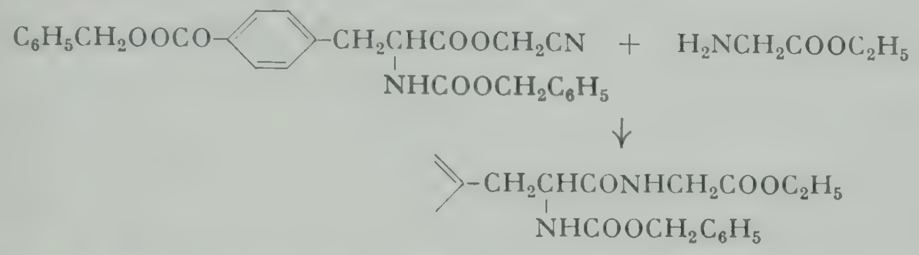
Halogenocarboxylic acid amides

s. *7*, 425

Activated carboxylic acid esters as mild acylating agents

Subst. carboxylic acid amides

99.

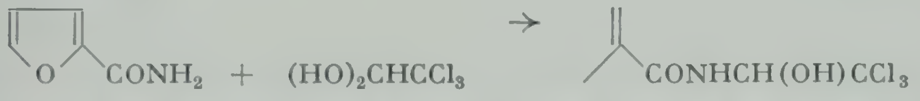


Peptides. A mixture of N,O-dicarbobenzoxy-L-tyrosine cyanomethyl ester, glycine ethyl ester, and ethyl acetate kept 8 hrs. at room temp. → N,O-dicarbobenzoxy-L-tyrosylglycine ethyl ester. Y: 94%.—Aminolysis by ar. and sec. amines proceeds only slowly but can be greatly facilitated by the catalytic action of strong tert. amines and of acids. F. e. s. R. Schwyzer, M. Feurer, and B. Iselin, Helv. *38*, 83, 1508 (1955); cf. M. Bodánsky, Nature *175*, 685 (1955).

Chloralamides

←

0.



A mixture of 2-furamide and anhydrous chloral gently refluxed 10 min. until solid begins to separate → 1-(2-furamido)-2,2,2-trichloroethanol. Y: 86%. F. e. and reactions s. J. R. Willard and C. S. Hamilton, Am. Soc. *75*, 2370 (1953).

Carboxylic acid alkoxymethylamides via acylaminomethylpyridinium salts

←

s. *8*, 437

Dicarboxylic acid amide esters from dicarboxylic acid esters

COOR → CON<

s. *6*, 844; also diamides s. *8*, 438

Dicarboxylic acid imides

○

from dicarboxylic acids

s. *8*, 439/40

from dicarboxylic acid esters

s. *9*, 435

from dicarboxylic acid anhydrides – Phthalimides

s. *5*, 341; s. a. O. Neunhoeffer and H. Ulrich, B. *88*, 1123 (1955)

Iminoesters from orthocarboxylic acid esters

$C(OR)_3 \rightarrow C(:NR')OR$

s. *8*, 441

Carboxylic acid hydrazides COOR → $CONHNH_2$
from carboxylic acid esters
s. *8*, 515; *9*, 476

also with simultaneous hydantoin ring opening
s. *9*, 436

Hydrazides difficult to prepare
s. *7*, 426

Carboxylic acid amide hydrazides ←
from dicarboxylic acid esters via dicarboxylic acid amide esters
s. *6*, 398

Diacylhydrazines AcNHNHAc
s. *9*, 437

Formamidines from N-subst. iminoesters NHCH:NR
s. *6*, 399

N,N′-Dicarbamylformamidines RNHCON:CH·NHCONHR
s. *9*, 438

Acylguanidines ←
s. *9*, 439

N-Acylsulfoximines from sulfoximines ←
s. *8*, 442

Replacement of cyclic oxygen by cyclic nitrogen

Lactams from lactones
s. *10*, 529

Imidocarboxylic acids from aminocarboxylic acids
s. *10*, 443

in pyrylium salts
s. *2*, 366; s. a. L. C. King and F. J. Ozog, J. Org. Chem. *20*, 448 (1955)

Enaminolactams from ketocarboxylic acids

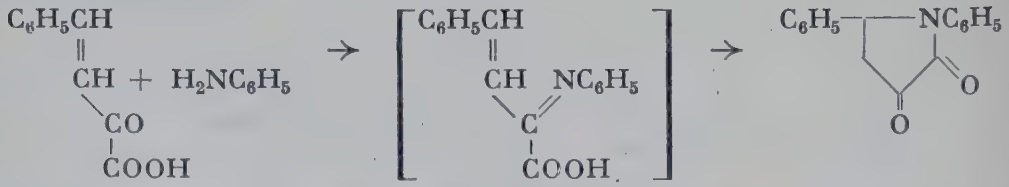
s. *9*, 440

Pyrrole ring s. *6*, 401

N-Subst. 2-pyrrolidones s. *6*, 402

2,3-Pyrrolidiones

301.



A soln. of aniline in abs. ethanol added dropwise with stirring to a soln. of benzylidenepyruvic acid in the minimum amount of ethanol, allowed to stand ca. 0.5 hr. until no more precipitation occurs, more ethanol added, and refluxed 0.5 hrs. whereby the rearrangement is completed → 1,5-diphenyl-2,3-pyrrolidinedione. Y: 79%. F. e. and methods s. W. R. Vaughan and L. R. Peters, J. Org. Chem. *18*, 382 (1953).

Reactions with azeotropic water entrainment
(1,3-Di-N)-heterocyclics
s. *6*, 405

Pyrazoles from β-diketones
s. *6*, 403

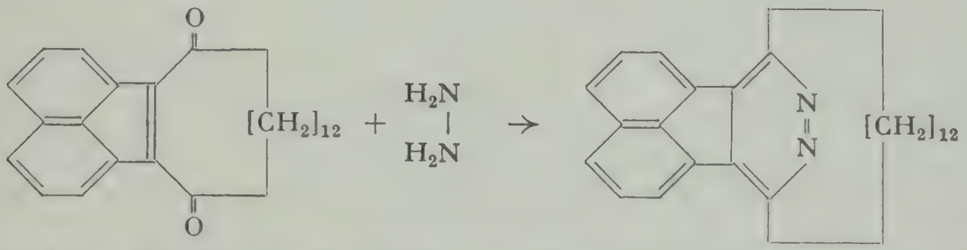
Pyrazolines from α,β-ethyleneketones
s. 8, 927; s. a. L. Mehr, E. I. Becker, and P. E. Spoerri, Am. Soc. *77*, 984 (1955)

Imidazolidines	**Benzimidazoles**
s. *6*, 404	s. *8*, 443

Pyridazines from 2,5-diacoxy-2,5-dihydrofurans
s. *7*, 427

Pyridazine ring ←

02.



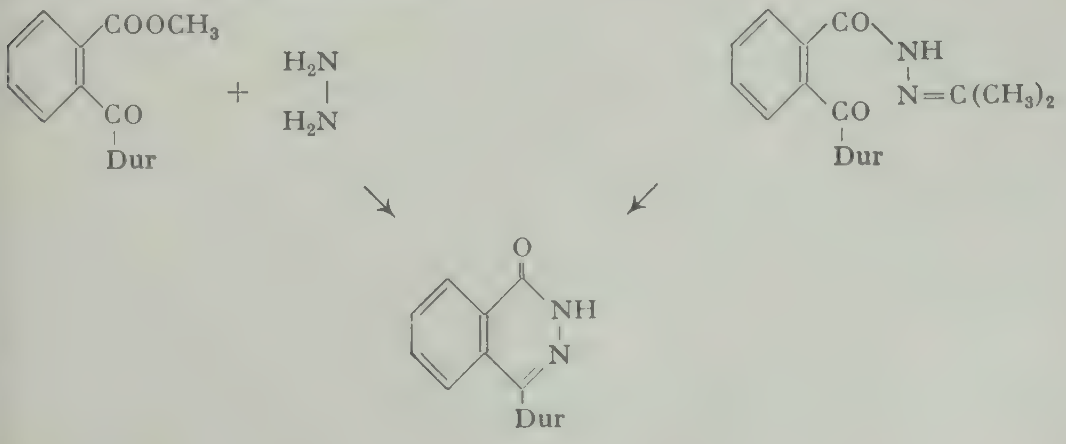
A mixture of 7-20-tetradecahydrocyclohexadeca[1,2-a]acenaphthylen-7,20-dione (prepn. s. 208), 90%-hydrazine hydrate, and butanol heated 2 hrs. on a steam bath → 21,22-diaza-8-19-dodecahydro-7,20-ethenocyclohexadeca[1.2-a]acenaphthylene. Y: 86%. F. e. s. C. F. H. Allen and J. A. VanAllan, J. Org. Chem. *18*, 882 (1953).

2,3,4,5-Tetrahydro-3-cyanopyridazines
s. *8*, 444

Pyridazinones and phthalazones
s. 7, 428; phthalazones s. *8*, 445

Phthalazones from o-ketocarboxylic acid esters and o-ketoacylhydrazones

3.



Steric hindrance. Hindered carbonyl groups unreactive in intermolecular reactions may, however, undergo *intramolecular* reactions.—E:

A soln. of methyl o-duroylbenzoate and 85%-hydrazine hydrate in ethanol refluxed 2 days	A soln. of 1-(o-duroylbenzoyl)-2-isopropylidenehydrazine in ethanol containing glacial acetic acid refluxed 2 hrs.

Y: 93%. 1-duryl-4-phthalazone. Y: 75%.

F. e. s. R. C. Fuson and W. C. Hammann, Am. Soc. *74*, 1626 (1952); s. a. *10*, 357.

Tetrahydropyrimidines from carboxylic acid esters
s. *7*, 429

Quinazolines
s. *7*, 430; from iminoesters s. *7*, 431

4-Quinazolones
s. *8*, 446

Quinazolones from 3,1,4-benzoxazones
s. *6*, 406

2,3-Piperazinediones
s. *6*, 408

3,5-Piperazinediones
s. *9*, 441

1-Hydroxy-2-pyrazinones from hydroxamic acids
s. *9*, 442

2,3-Dihydroxyquinoxalines
s. *6*, 407

Quinoxaline-2-carboxylic acid ureides
s. *8*, 447

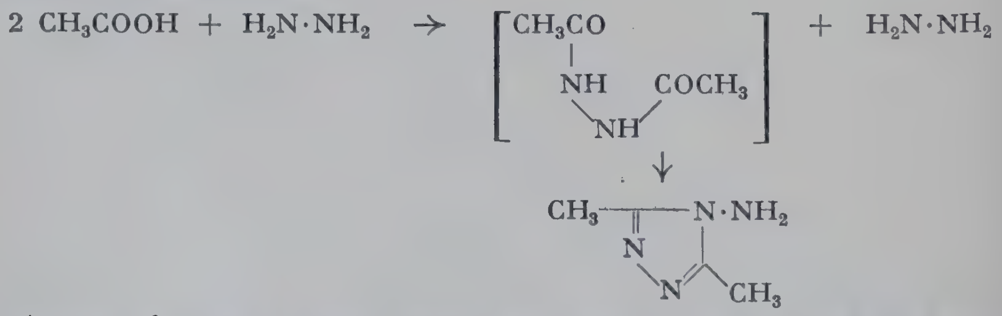
3,4-Dihydro-2-quinoxalones
s. *8*, 563

Photoreduction – 1,4-Oxazine ring
s. *6*, 383

1,2,4-Triazoles from carboxylic acid hydrazides and isothioureas via acylaminoguanidines
s. *6*, 409

4-Amino-1,2,4-triazoles

304.



A mixture of 1 mole glacial acetic acid and 1.5 moles 85%-hydrazine hydrate soln. heated slowly in an oil-bath to 220-230° where it is maintained for 5 hrs. → 4-amino-3,5-dimethyl-1,2,4-triazole. Y: 75%.—Higher molecular weight aminotriazoles can be prepared by heating diacyl hydrazides and hydrazine hydrate soln. in a sealed tube. F. e. s. R. M. Herbst and J. A. Garrison, J. Org. Chem. *18*, 872 (1953).

3,5,7-Triazatricyclo[3.3.1.1$^{3.7}$]decanes
s. *8*, 448

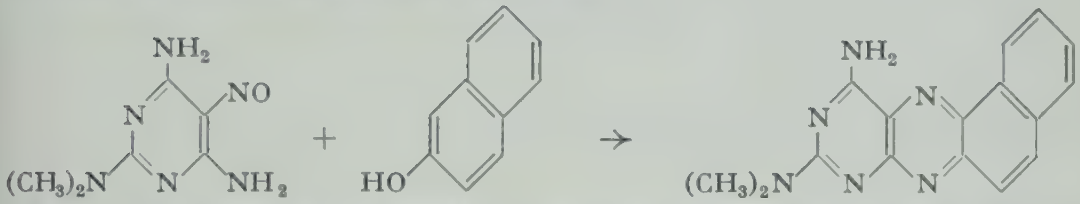
Reactions with tris(hydroxymethyl)aminomethane
1-Aza-3,7-dioxabicyclo[3.3.0]octanes
s. *8*, 449

1,2,4-Oxadiazoles
s. *4*, 362; s. a. K. Clarke, Soc. *1954*, 4251

Benzo-1,2,4-thiadiazine 1,1-dioxides
s. *7*, 467; *8*, 452

5,7,9,10-Tetraaza-1,2-benzanthracenes

05.

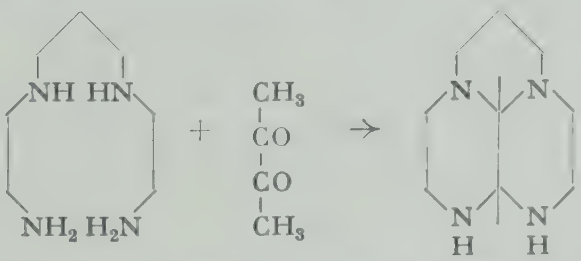


1.8 g. 4.6-diamino-2-dimethylamino-5-nitrosopyrimidine added all at once with stirring at 130° to molten 2-naphthol, the temp. slowly raised to 150° when a vigorous reaction occurs, and the product isolated after the reaction has subsided → 2.24 g. 8-amino-6-dimethylamino-5.7,9.10-tetraaza-1,2-benzanthracene. F. e. s. D. G. I. Felton, T. S. Osdene, and G. M. Timmis, Soc. *1954*, 2895.

s-Triazolo[3,4-a]phthalazines
s. *7*, 432

Naphthopiperazines from α-diketones

6.



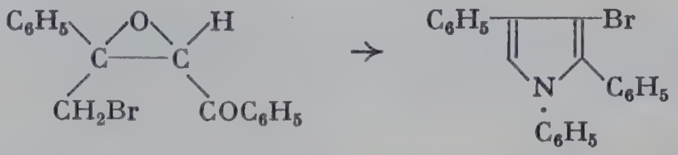
Azeotropic water entrainment. Diacetyl added gradually to a mixture of N,N′-bis-(2-aminoethyl)-1,3-diaminopropane and benzene, then refluxed with a water separator until no more water is collected → 1,8-trimetyhlene-9,10-dimethylnaphthopiperazine. Y: 71.4%. F. e. s. H. Stetter. B. *86*, 69 (1953).

N-Condensed heterocyclics – Polyazaindolizines
s. *7*, 433

Pyrazoles from O-heterocyclics ←
Amines from hydrazones
s. *9*, 444

Pyrroles from α,β-oxidoketones ←
Reactions with diphenacyl halides

307.

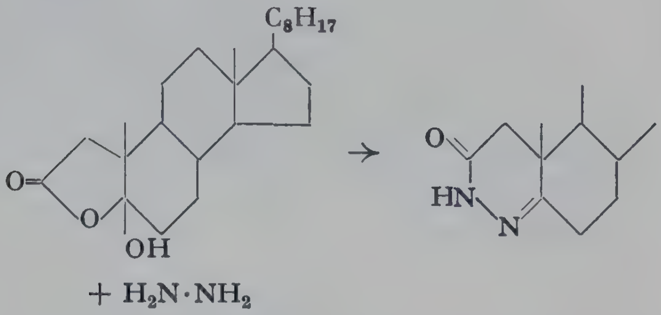


Stereospecific reactions. A mixture of α-diphenacyl bromide and aniline heated until effervescence takes place, then refluxed 15 min. → 3-bromo-1,2,4-triphenylpyrrole. Y: 77%.—The β-isomer, which has a *cis*-arrangement of the phenyl and benzoyl groups, gives 3-hydroxy-1,2,4-triphenylpyrrole. H. H. Wasserman and J. B. Brous, J. Org. Chem. *19*, 515 (1954); f. reactions with diphenacyl halides s. C. L. Stevens, R. J. Church and V. J. Traynelis, J. Org. Chem. *19*, 522, 533 (1954).

Pyridine from furan ring – 3-Hydroxypyridines
s. *9*, 443; s. a. B. *88*, 178 (1955)

Pyridazinone ring

308.



Hydrazine hydrate added to an alc. soln. of lactol, and refluxed 4 hrs. → pyridazinone. Y: 88%. F. L. Weisenborn, D. C. Remy, and T. L. Jacobs, Am. Soc. *76*, 552 (1954).

Oxazolidines from oxido compounds
s. *9*, 445

Sodium hydride *NaH*
Thiouracils ○
β-Ketocarboxylic acid esters from carboxylic acid esters
C^{14}-compounds s. *7*, 434

Sodium hydroxide *NaOH*
Oximes CO → C:NOH
Aldoximes s. *6*, 411; ketoximes s. M. C. Kloetzel, J. E. Little, Jr., and D. M. Fisch, J. Org. Chem. *18*; 1511 (1953)

α-Oximinocarboxylic acids
s. *10*, 567

Acylamines from amines NH → NAc
Optically active compounds s. *6*, 412

Acetylation of α-aminocarboxylic acids under non-racemizing conditions
s. *8*, 451

Carboxylic acid amides via mixed carboxylic acid anhydrides COOH → CONHR
Peptides s. *7*, 436

Pyrazoles from β-diketones ○
s. *7*, 437

2-Hydroxypyrazines
s. *5*, 286; s. a. G. P. G. Dick and H. C. S. Wood. Soc. *1955*, 1379

Hexahydro-1,3,5-triazines from aminomethylol sulfites
s. *7*, 438

Benzo-1,2,4-thiadiazine 1,1-dioxides
s. *8*, 452

Pyrimido[4,5-b]pyrazines
s. *6*, 413; s. a. Chem. and Ind. *1954*, 1585

Potassium hydroxide *KOH*

Aminomethylene from hydroxymethylene compounds C:C·OH → C:C·N<
s. *6*, 511

Guanylhydrazones from aldehydes CHO → $CH{:}NNHC({:}NH)NH_2$
s. *8*, 453

1,2-Dihydro-3,1-benzoxazines ○
s. *9*, 446

Potassium hydroxide/alcohol

Pyrimidines from amidines and α,β-ethyleneketones via dihydropyrimidines
s. *8*, 454

Sodium/alcohol *NaOR*

Alkoximes from isomeric oximes C:NOH → C:NOR
s. *6*, 462

Carboxylic acid amides from carboxylic acid esters COOR → $CONH_2$
s. *6*, 414

Hydroxamic acids from carboxylic acid esters COOR → CONHOH
s. *8*, 455

3,5-Pyrazolidione ring from malonic acid esters

s. *7*, 439; also labeled compounds s. Can. J. Chem. *32*, 823 (1954) 1,3-dioxopyrazolidino[1,2-f]benzo[c′]cinnolines s. H. Kühne and H Erlenmeyer, Helv. *38*, 531 (1955)

4,6-Dihydroxypyrimidines
s. *8*, 456

5-Carbethoxyuracils
s. *9*, 447

Pyrimidines from amidines
s. *8*, 457

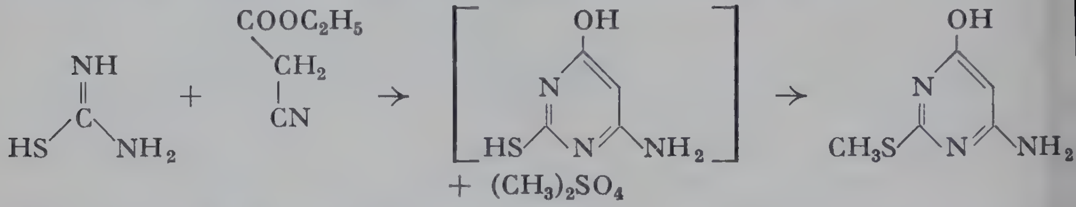
5-Amino- via 5-nitroso-pyrimidines
s. *9*, 448

Pyrimidines from guanidines
s. *8*, 458

2,4-Diamino-6-hydroxypyrimidines
s. *8*, 459

Pyrimidine ring synthesis with subsequent S-alkylation

309.



Ethyl cyanoacetate and thiourea added to a soln. of Na-methoxide in abs. alcohol, refluxed 2 hrs. with stirring, after addition of water treated dropwise during 5 min. with dimethyl sulfate at such a rate that the soln. refluxes gently, stirring and refluxing continued for 10 min. → 2-methylmercapto-4-amino-6-pyrimidol. Y: 82%. B. R. Baker, J. P. Joseph, and R. E. Schaub, J. Org. Chem. *19*, 631 (1954); f. S-methylations s. J. Org. Chem. *19*, 638.

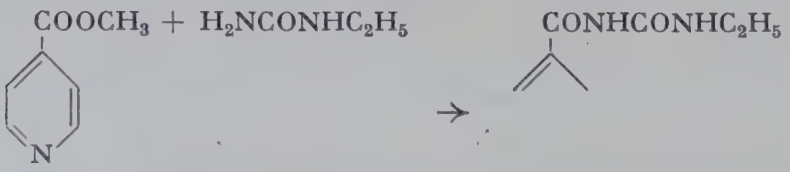
Barbituric acids
s. *7*, 440; with simultaneous deacetylation s. *7*, 441

5-Subst. 1-arylamino-4-iminobarbituric acids from semicarbazides
s. *8*, 460

Sodium/liq. ammonia *Na/NH₃*

Acylureas from carboxylic acid esters NHCONH₂ → NHCONHCOR

310.



Na added in small pieces to a well stirred soln. of monoethylurea in liq. NH_3, then methyl isonicotinate added rapidly, and the NH_3 boiled off → 1-isonicotinyl-3-ethylurea. Y: 75%. F. e. s. A. Stempel, J. Zelauskas, and J. A. Aeschlimann; J. Org. Chem. *20*, 412 (1955).

Sodium carbonate *Na_2CO_3*

Oximes from ketones CO → C:NOH

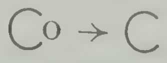
s. *8*, 195; *9*, 36

Hydrazones C:NNHR

s. *10*, 325

Imidazolones from oxazolones

s. *7*, 442



1,2,4-Triazoles from acylaminoguanidines ○

s. *8*, 461

Sodium hydrogen carbonate *$NaHCO_3$*

Acylhydrazones CO → C:NNHAc

s. *7*, 387

Potassium carbonate *K_2CO_3*

Enamines from enolethers C:C·OR → C:C·N<

s. *7*, 443

Thiouracils ○

s. *8*, 462

Sodium formate *HCOONa*

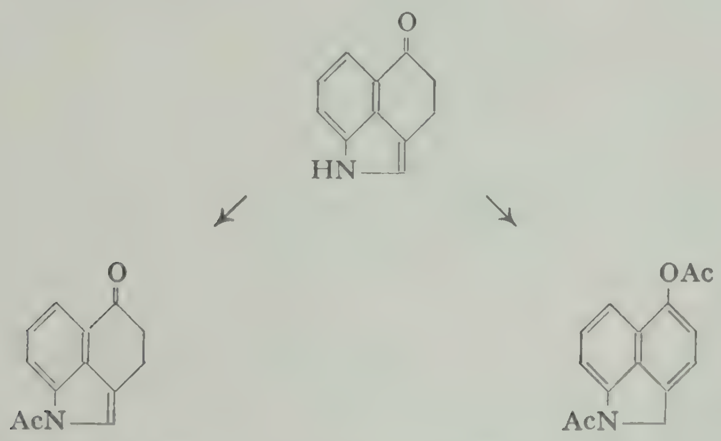
Formamides NH → NCHO

s. *7*, 520

Alkali acetate ←

Acylation, ←

also with formation of a naphthalene from an indole ring
by migration of a carbon-carbon double bond
Phenol acetates from cyclic ketones
Cation specificity



A soln. of 5-oxo-1,3,4,5-tetrahydrobenz[cd]indole in acetic anhydride containing

Na-acetate refluxed 2,5 hrs. → 1-acetyl-5-oxo-1,3,4,5-tetrahydrobenz[cd]-indole. Y: 85%.	K-acetate refluxed 5 hrs. → 1-acetyl-5-acetoxybenz[cd]indoline. Y: 68%.

Li-acetate gives a molecular compound of both products in 84% yield. C. A. Grob and P. Payot, Helv. *36*, 839 (1953).

Sodium acetate *CH_3COONa*

Oximes from ketones CO → C:NOH
s. *7*, 444

O-Alkoximes CO → C:NOR
s. *8*, 463; s. a. F. Nerdel and J. Huldschinsky, B. *86*, 1005 (1953)

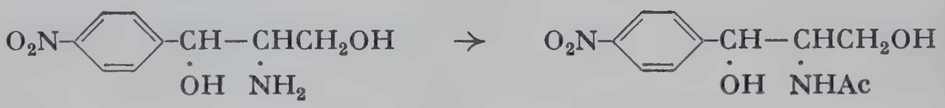
p-Sulfophenylhydrazones CO → C:NNHR
s. *8*, 464

Aldehyde acylhydrazones from prim. alcohols CH_2OH → CH:NNHAc
s. *8*, 465

Thiosemicarbazones CO → $C:NNHCSNH_2$
s. *9*, 432

Selective N-acylation NH → NAc

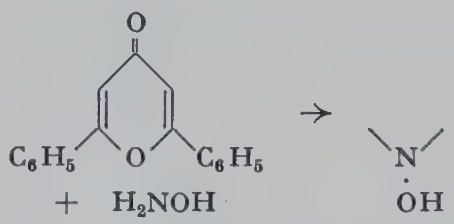
312.



Acetic anhydride added to a thick slurry of 75 g. D-(–)-*threo*-2-amino-1-p-nitrophenylpropane-1,3-diol, Na-acetate, and crushed ice, then vigorously shaken for 60 min. → 61 g. D-(–)-*threo*-2-acetamido-1-p-nitrophenylpropane-1,3-diol. D. D. Evans et al., Soc. *1954*, 1687.

1-Hydroxy-4-pyridones from 4-pyrones ←

313.



An alc. soln. of 2,6-diphenylpyrone heated 6 hrs. with hydroxylamine hydrochloride and Na-acetate in water → 1-hydroxy-2,6-diphenyl-4-pyridone. Y: 50%. F. e. s. G. Soliman and I. El-Sayed El-Kholy, Soc. *1954*, 1755.

Pyrrole ring ○
s. *7*, 445

1,2,4-Triazoles from hydrazines
Einhorn-Brunner ring closure
s. *9*, 449

Sodium acetate/hydrochloric acid *CH_3COONa/HCl*

N-Acetylation NH → NAc
s. *8*, 466

Reactions under physiological conditions ○
Benzimidazoles
s. *8*, 815

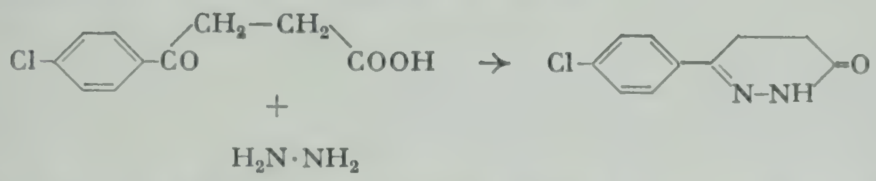
Sodium hydrogen sulfite *$NaHSO_3$*
N-Acylation with peroxycarboxylic acids NH → NAc
s. *9*, 450

Quinoxaline ring ○
s. *7*, 446

Potassium iodide *KI*
Sec. from prim. amines and hydroxy compounds NH_2 → NHR
s. *9*, 451

Potassium salt *K^+*
Pyridazinones from γ-ketocarboxylic acids ○

314.



A soln. of 10-15% excess hydrazine sulfate in 1 equivalent *N* KOH added at 80-90° to a soln. of 4-(4′-chlorophenyl)-4-oxobutanoic acid in 1 equivalent *N* KOH, and refluxed 1-2 hrs. on a steam bath → 6-(4′-chlorophenyl)-4,5-dihydro-3-pyridazone. Y: 88%. F. e. s. E. A. Steck, R. P. Brundage, and L. T. Fletcher, Am. Soc. *75*, 1117 (1953).

Trialkylamine *R_3N*
Carboxylic acid amides from carboxylic acids COOH → CON<
via mixed alkoxyformic acid anhydrides

Peptides
s. *7*, 447; oxytocin synthesis s. Helv. *38*, 1491 (1955)

Triethylamine *$(C_2H_5)_3N$*
s. *9*, 452; s. a. A. R. Battersby and J. C. Robinson, Soc. *1955*, 259

Dicarboxylic acid amide esters
s. *9*, 452

Peptides and carboxylic acid esters
via mixed carboxylic acid anhydrides
s. *9*, 453; s. a. S.-C. J. Fu, S. M. Birnbaum, and J. P. Greenstein, Am. Soc. *76*, 6054 (1954)

Carboxylic acid acylthioethylamides from carboxylic acids
via mixed alkoxyformic acid anhydrides
and carboxylic acid ethylenimides
s. *9*, 454

Piperidine *$C_5H_{11}N$*

1,1-Aminohydroxy from 1,1-dihydroxy compounds $C(OH)_2 \rightarrow C(OH)N<$
s. *6*, 418

Pyrimidines from amidines ○
s. *9*, 455

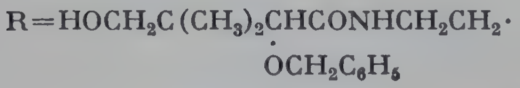
Dihydro-1,3,5-triazines from biguanides
s. *8*, 467

N-Methylmorpholine ←

Carboxylic acid amides from carboxylic acids via mixed alkoxyformic acid anhydrides $COOH \rightarrow CON<$

315. $R\cdot COOH + ClCOOC_2H_5 \rightarrow [R\cdot CO\cdot O\cdot OC\cdot OC_2H_5] + H_2NCH_2CH_2SCH_2C_6H_5$

$$\downarrow$$



$R{=}HOCH_2C(CH_3)_2\underset{OCH_2C_6H_5}{\overset{}{CH}}CONHCH_2CH_2\cdot$

$R\cdot CONHCH_2CH_2SCH_2C_6H_5$

Ethyl chloroformate added dropwise to a soln. of pantothenic acid 2′-benzyl ether (prepn. s. 263) and 4-methylmorpholine in dry dimethylformamide cooled to -20°, the temp. kept 10 min. at -5° after the addition, then a soln. of 2-benzylthioethylamine in chloroform cooled to -5° added, the temp. kept 15 min. at -5° and 12 hrs. at room temp. → pantheteine $O^{2'}S$-dibenzyl ether. Y: 87%. J. Baddiley and E. M. Thain, Soc. *1953,* 1610.

Aniline *$C_6H_5NH_2$*

Osazones ←
s. *6*, 416

Pyridine *C_5H_5N*

Acylamines $NH_2 \rightarrow NHAc$
s. *7*, 398

Diacylamines $N(Ac)_2$
s. *6*, 417

Pyridine/phosphorus trichloride *C_5H_5N/PCl_3*
s. Phosphorus trichloride/pyridine

Silver acetate *CH_3COOAg*

N-Acetylation $NH \rightarrow NAc$
s. *9*, 876

Calcium oxide *CaO*

Hydrazones from ketones $CO \rightarrow C{:}NNH\cdot$
s. *6*, 450

Barium carbonate *$BaCO_3$*

Oximes from ketones $CO \rightarrow C{:}NOH$
s. *7*, 448

Zinc/acetic acid *Zn/CH$_3$COOH*

Nitrones from aldehydes and nitro compounds C:N(O)R
Isaldoximes
s. *6*, 419

Alkylmagnesium iodide *RMgI*

Carboxylic acid amides from carboxylic acid esters COOR → CON<
Bodroux reaction
s. *9*, 456

Magnesium chloride *MgCl$_2$*

Tert. amines from oxo compounds CO → CHNR$_2$
Extension of the Leuckart synthesis
s. *9*, 457

Zinc chloride *ZnCl$_2$*

Azomethines from ketones CO → C:NR
Azeotropic water entrainment s. *10*, 703

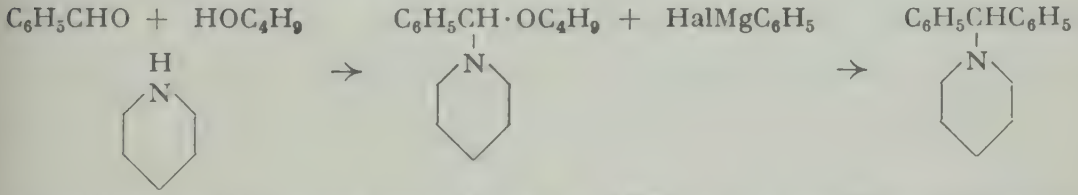
Zinc chloride/ammonium chloride *ZnCl$_2$/NH$_4$Cl*

Imidazolines from nitriles and aminoalcohols ○
s. *9*, 458

Mercuric chloride *HgCl$_2$*

Synthesis of tert. amines from aldehydes via 1-aminoethers ←
Replacement of alkoxy groups by hydrogen

16.



A mixture of 0.2 mole benzaldehyde, 0.22 mole piperidine, 1.0 mole 1-butanol, a substantial excess of Ca-sulfate (Drierite), and a small amount of mercuric chloride stirred 24-48 hrs. at room temp. → (α-piperidylbenzyl) butyl ether (Y: 80%) in an equal volume of ether added slowly to phenyl-MgBr prepared from 1.5 mole phenyl bromide and 2 mole Mg turnings, stirred 12-24 hrs. at room temp. → N-benzhydrylpiperidine (Y: 99%).—*Reduction* occurs with *tert*-butyl-MgCl, whereby the butoxy group is replaced by hydrogen. The same product can be obtained by hydrogenation with PtO$_2$. F. e. s. A. T. Stewart, Jr., and C. R. Hauser, Am. Soc. 77, 1098 (1955).

Aluminum *Al*

Amines from oxo compounds CO → CHNHR
s. *9*, 459

Boric acid/borax *HBO$_2$/Na$_2$B$_4$O$_7$*

Peptide synthesis from acylphosphoric acid esters CONHR
s. *7*, 449

Bauxite *Al_2O*

N-Alkylation of amines with alcohols ←
Nitriles from carboxylic acids
s. *6*, 420

Bentonite ←

Alkylation of amines with alcohols NH → N

317. $C_6H_5NH_2 + HOC_2H_5 \rightarrow C_6H_5NHC_2H_5$

Aniline allowed to react with 2 parts of ethanol over bentonite (Al silicate) at 350° and a space velocity of 0.15 → ethylaniline. Y: 87% M. B. Turova-Pollak, N. V. Borunova, and E. S. Semenova, Ж. *23* 1024 (1953); C. A. *48*, 8747h.

Ammonium carbonate *$(NH_4)_2CO_3$*

Replacement of cyclic oxygen by cyclic nitrogen
s. *8*, 468

Dicarboxylic acid imides from dicarboxylic acids
s. *7*, 881

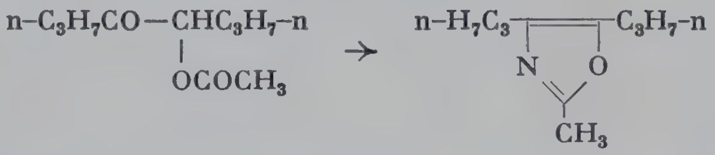
Ammonium formate *$HCOONH_4$*

Prim. amines from ar. aldehydes $CHO \rightarrow CH_2NH_2$
Leuckart reaction
s. *7*, 450

Ammonium acetate *CH_3COONH_4*

Oxazoles from α-acoxyketones

318.



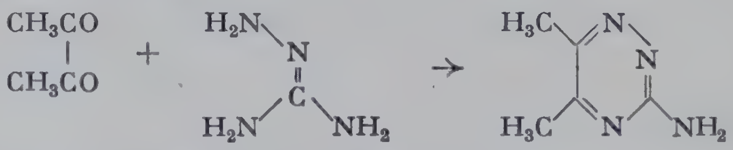
Butyroin acetate and NH_4-acetate in glacial acetic acid refluxed 1 hr. → 2-methyl-4,5-di-n-propyloxazole. Y: 85%. F. e. and methods s. G. Theilig, B. *86*, 96 (1953).

Pyridine from furan ring ←
3-Hydroxy-2-arylpyridines s. *8*, 469

Hydrogen carbonates ←

3-Amino-1,2,4-triazines

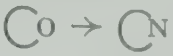
319.



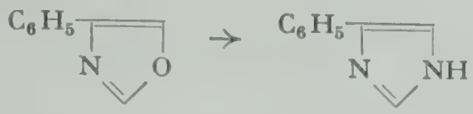
An aq. soln. of biacetyl added at 25° to a suspension of aminoguanidine bicarbonate in water, allowed to stand 22 hrs. at the same temp., then warmed to 50° for 1 hr. → crude 3-amino-5,6-dimethyl-1.2,4-triazine. Y: 82.6%. F. e. s. J. G. Erickson, Am Soc. *74*, 4706 (1952).

Formamide *$HCONH_2$*

Imidazoles from oxazoles



320.



4-Phenyloxazole boiled 3 hrs. with excess formamide → 4(5)-phenylimidazole. Y: 97%. F. e. s. G. Theilig, B. *86*, 96 (1953); with formamide/liq. NH_3 in an autoclave s. H. Bredereck, R. Gompper, and H. Wild, B. 88, 1351 (1955).

Formamide/formic acid *$HCONH_2/HCOOH$*

Amines from ketones $CO \rightarrow CHNH_2$

Modified Leuckart reaction

s. *8*, 470

Urea *$CO(NH_2)_2$*

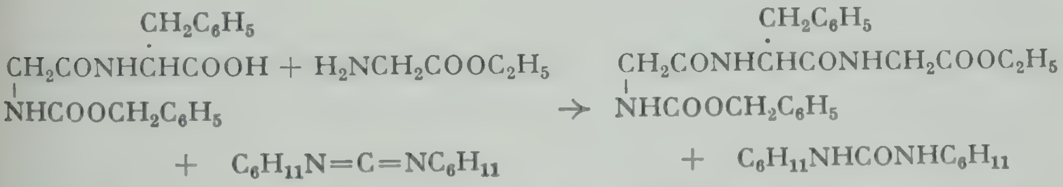
Dinitriles and cyanocarboxylic acids from dicarboxylic acids ←

s. *8*, 471

N,N'-Dicyclohexylcarbodiimide *$C_6H_{11}N{=}C{=}NC_6H_{11}$*

Subst. carboxylic acid amides from carboxylic acids COOH → CN<

21.



$$\begin{array}{l} \qquad\quad CH_2C_6H_5 \\ CH_2CONH\dot{C}HCOOH + H_2NCH_2COOC_2H_5 \\ | \\ NHCOOCH_2C_6H_5 \\ \qquad + \; C_6H_{11}N{=}C{=}NC_6H_{11} \end{array} \rightarrow \begin{array}{l} \qquad\quad CH_2C_6H_5 \\ CH_2CONH\dot{C}HCONHCH_2COOC_2H_5 \\ | \\ NHCOOCH_2C_6H_5 \\ \qquad + \; C_6H_{11}NHCONHC_6H_{11} \end{array}$$

Peptide. A soln. of carbobenzoxyglycyl-L-phenylalanine in tetrahydrofuran containing a slight excess of crystalline N,N-dicyclohexylcarbodiimide and ethyl glycinate allowed to stand 4 hrs. at room temp., then treated with a little acetic acid to decompose the excess reagent → carbobenzoxyglycyl-L-phenylalanylglycine ethyl ester. Y: 87%. F. e., also in methylene chloride, s. J. C. Sheehan and G. P. Hess, Am. Soc. *77*, 1067 (1955).

Papain ←

Subst. carboxylic acid hydrazides from carboxylic acids COOH → CONHNHR

Stereospecificity s. *7*, 451

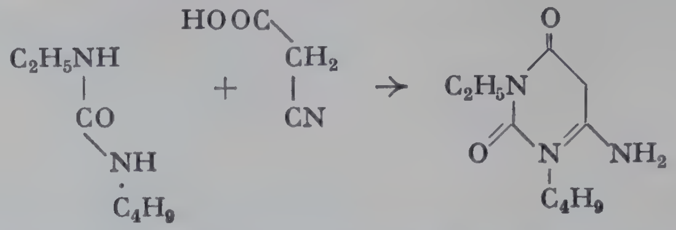
Acetic anhydride *$(CH_3CO)_2O$*

Selective formylation of amines $NH_2 \rightarrow NHCHO$

s. *8*, 472

6-Aminouracils – Modified Traube synthesis (

322.



1 mole each of N-butyl-N′-ethylurea and cyanoacetic acid heated 3 hr at 60° with 2 moles acetic anhydride in acetic acid → 1-butyl-3-ethy 6-aminouracil. Y: 70-90%.—This is the first step of a modified Traub synthesis of purine derivatives. F. e. s. J. H. Speer and A. L. Raymon Am. Soc. *75*, 114 (1953).

Pyrimidine ring closure
s. *6*, 421

Pyrimido[4,5-b]pyrazines from pyrazines
s. *8*, 473

Buffer pH 4.6-4.8 ←

N-Condensed heterocyclics
s. *8*, 571

Formic acid *HCOO*

Leuckart-Wallach reaction NH → N
Alkylation of amines with oxo compounds
s. *6*, 422

Clarke-Eschweiler reaction
Methylation of amines
s. *2*, 352; *4*, 378; s. a. D. J. Cram and B. L. Van Duuren, Am. Soc *77*, 3576 (1955)

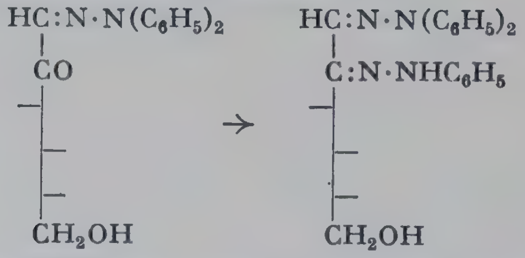
Amines from aldehydes
s. *6*, 423

Sym. ureas from alcohols and ureas $(RNH)_2C$
s. *9*, 460

Acetic acid *CH_3COOH*

Mixed osazones from osonehydrazones CO → C:NNH

323.



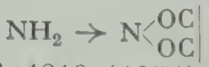
D-Fructosone diphenylhydrazone and phenylhydrazine in 50%-alcohol containing acetic acid heated several min. on a water bath → 1-diphenyl-2-phenyl-D-fructosazone. Y: 96%. F. e. s. G. Henseke and W. Liebenow, B. *87*, 1068 (1954).

Osazones and indole ring
from α-hydroxyketones and arylhydrazines ←
s. *7*, 452

Thiosemicarbazones CO → C:NNHCSNH$_2$
s. *6*, 424

from hydrazinium thiocyanate
s. *8*, 474

Phthalimides



$NH_2 \rightarrow N\left\langle\begin{matrix}OC\\OC\end{matrix}\right|$

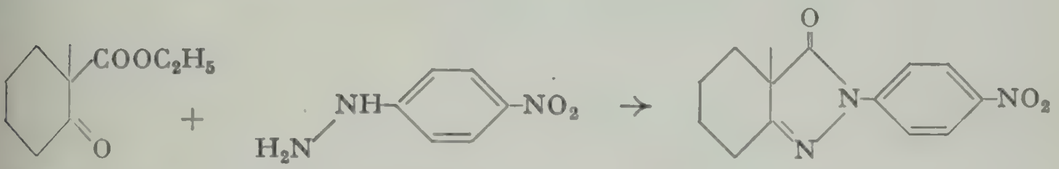
s. *1*, 332/3; s. a. R. C. Elderfield et al., Am. Soc. *77*, 4816, 4819 (1955)

Pyrroles from 2,4-dialkoxytetrahydrofurans ←
s. *9*, 461

Pyrazole ring from β-diketones ○
s. *6*, 403; dipyrazolyls s. J. L. Finar, Soc. *1955*, 1205

4,5,6,7-Tetrahydro-3-indazolones

324.



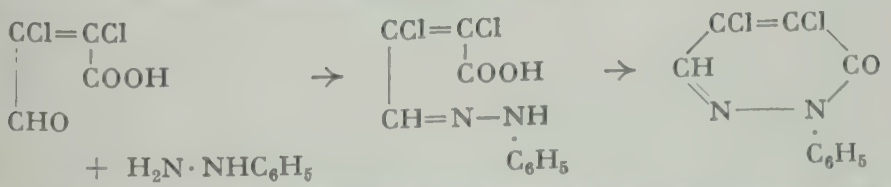
2-Methyl-2-carbethoxycyclohexanone and p-nitrophenylhydrazine in glacial acetic acid refluxed 20 min. → 2-(p-nitrophenyl)-9-methyl-4,5,6,7-tetrahydro-3-indazolone. Y: 87%. C. A. Grob and J. A. Rumpf, Helv. *37*, 1479 (1954).

Isoimidazoles **Benzimidazoles**
s. *9*, 462 s. *7*, 453

Stepwise degradation of peptides via 2-thiohydantoins
Elimination of terminal moieties
s. *8*, 475

Reactions with mucochloric acid
Pyridazinones from γ-oxocarboxylic acids

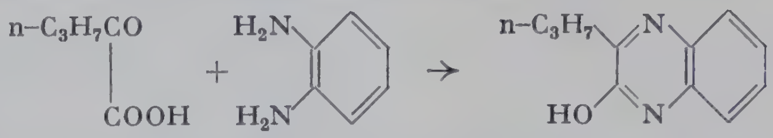
25.



A soln. of mucochloric acid and anhydrous Na-carbonate in cold water mixed with cold aq. phenylhydrazine hydrochloride, and the product isolated after 1 hr. → mucochloric acid phenylhydrazone (Y: ca. 100%) dissolved in glacial acetic acid and refluxed 15 min. → 4,5-dichloro-2-phenyl-3-pyridazone (Y: 90%). F. e. and reactions s. D. T. Mowry, Am. Soc. *75*, 1909 (1953).

2-Hydroxyquinoxalines
in identification of α-ketocarboxylic acids

326.



Aq. α-ketovaleric acid added slowly with stirring to a soln. of exce o-phenylenediamine in 10%-acetic acid, and the product isolated aft standing 5 hrs. → 3-n-propyl-2-quinoxalinol. Y: 82%. F. e. s. D. Morrison, Am. Soc. *76*, 4483 (1954); in alcohol s. P. H. Gore and G. Hughes, Am. Soc. *77*, 5738 (1955).

7,8-Dihydropyrimido[4,5-b]pyrazines
s. *8*, 476

Nitrobenzene C_6H_5N

N-Subst. 4-aminoquinolines
from 4-keto-1,2,3,4-tetrahydroquinolines
←

s. *9*, 463

Silica *Si*

Nitriles from carboxylic acids
COOH → C

327. $HOOC[CH_2]_7COOH \rightarrow NC[CH_2]_7CN$

General method. Azelaic acid allowed to react at 500° with anhydrou NH_3 in a Pyrex tube filled with silica gel → azelanitrile. Y: 63-68% A. C. Cope, R. J. Cotter, and L. L. Estes, Org. Synth. *34*, 4 (1954) labeled compounds s. W. R. Vaughan and D. J. McCane, Am. Soc. *7* 2504 (1954).

Sodium azide *NaN*

Phenanthridines from quinones
←

s. *6*, 425

Hydrazoic acid *HN*

Nitriles from aldehydes
CHO → C

s. *10*, 164

Tetraethyl pyrophosphite $(C_2H_5O)_2POP(OC_2H_5)$

Subst. carboxylic acid amides
from carboxylic acids
Peptide synthesis
COOH → CON<

s. *9*, 464; oxytocin synthesis s. R. A. Boissonnas et al., Helv. *38*, 149 (1955)

Dialkyl chlorophosphate $(RO)_2POC$

Alkylation of amines
NH → N

s. *9*, 465; cf. W. Gerrard and G. J. Jeacocke, Chem. & Ind. *1954*, 153

Phosphoric acid *H_3PO_4*

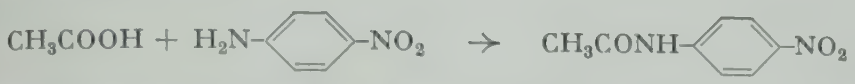
2,4-Dinitrophenylhydrazones CO → C:NNHR
s. *9*, 466

Subst. carboxylic acid hydrazides from carboxylic acid esters COOR → CONHNHR
s. *9*, 467

Polyphosphoric acid *$H(PO_3H)_xOH$*

Subst. carboxylic acid amides from carboxylic acids COOH → CON<

28.



Polyphosphoric acid added to a mixture of acetic acid and p-nitraniline, then heated to 160° during 20 min. → p-nitroacetanilide. Y: 67%. F. e. s. H. R. Snyder and C. T. Elston, Am. Soc. *76*, 3039 (1954).

Phosphorus trichloride *PCl_3*

s. *6*, 884; s. a. J. Indian Chem. Soc. *31*, 108 (1954)

Peptides
s. *6*, 426

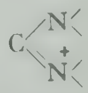
Phosphorus trichloride/pyridine *PCl_3/C_5H_5N*

Carboxylic acid amides from carboxylic acids and phosphazo compounds
Peptides s. *9*, 468

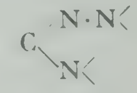
Phosphorus oxychloride *$POCl_3$*

Azomethines from amines and oxo compounds $CO + H_2N \rightarrow C{:}N$
s. *7*, 454

Amidinium salts from carboxylic acid amides
s. *6*, 427



Amidrazones from carboxylic acid amides and hydrazines
s. *6*, 428



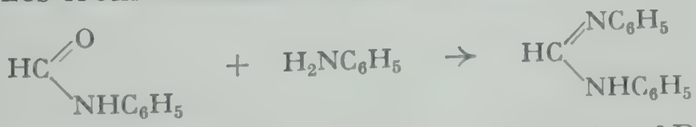
Phosphorus oxychloride/phosphorus pentachloride *$POCl_3/PCl_5$*

Nitriles from carboxylic acids COOH → CN
s. *6*, 429

Phosphorus pentachloride *PCl_5*

Formamidines from formamides and amines ←

9.



$$HC(=O)NHC_6H_5 + H_2NC_6H_5 \rightarrow HC(=NC_6H_5)NHC_6H_5$$

Formanilide added in small portions to a cooled soln. of PCl_5 in chloroform, on cessation of the reaction a chloroform soln. of aniline added, refluxed 2.5 hrs. with agitation, and the crude hydrochloride converted to the free base by adding it to a soln. of Na-ethoxide in ethanol → N,N′-diphenylformamidine. Y: 66%. F. e. s. H. G. Mandel and A. J Hill, Am. Soc. *76*, 3978 (1954).

Phosphorus pentachloride/p-toluenesulfonic acid amide $PCl_5/TsNH$

Nitriles from carboxylic acids COOH → CN
s. *6*, 430

Sulfamide/pyridine $SO_2(NH_2)_2/C_5H_5N$

Carboxylic acid amides from carboxylic acids COOH → $CONH_2$
s. *6*, 431

Sulfates of organic bases ←

Pyrimido[4,5-b]pyrazines ○
s. *7*, 455

Dimethylformamide-sulfur trioxide complex $HCON(CH_3)_2,SO_3$

Peptides COOH → CONHR
s. *6*, 432

p-Toluenesulfonic acid TsOH

Sec. from prim. amines and p-toluenesulfonic acid esters OTs → NHR
Aminosteroids s. *8*, 477

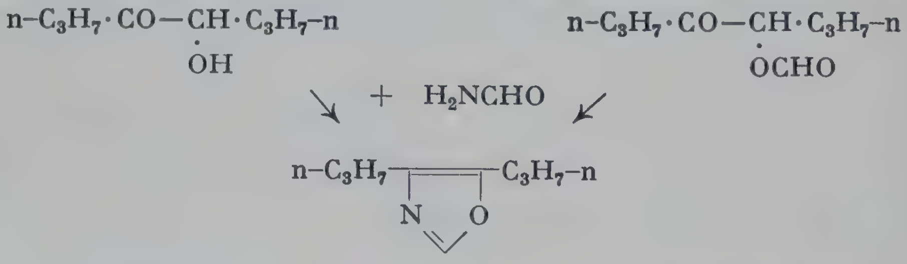
Sulfuric acid H_2SO_4

Monosubst. ureas from alcohols OH → $NHCONH_2$
s. *6*, 433

1,1-Di(sulfonylamides) $C(NHSO_2R)_2$
s. *7*, 456

Oxazoles from α-hydroxy- and α-formoxy-ketones ○

330.



Butyroin, formamide, and concd. H_2SO_4 heated slowly with stirring, kept 1 hr. at 100° and 2.5 hrs. at 150° | Butyroin formate, formamide, and formic acid refluxed 2 hrs.

Y: 65%. 4,5-di-n-propyloxazole. Y: 75%.
F. e. s. H. Bredereck and R. Gompper, B. *87*, 726 (1954).

1,3-Benzoxaz-4-ones
s. *7*, 457

Pyrimido[4,5-b]pyrazines
s. *7*, 458

Iodine I

Sec. from prim. amines and phenols NH_2 → NHR
s. *9*, 713

Oxazolidines from 2-aminoalcohols ○
s. *9*, 469

Perchloric acid *$HClO_4$*

Pyridine from pyrone ring – Baeyer reaction ←
s. *6*, 434

Ammonium chloride *NH_4Cl*

Partial replacement of hydroxyl by amino groups $OH \rightarrow NH_2$
s. *8*, 478

Glycosaminides $OH \rightarrow N\langle$
s. *9*, 470; s. a. R. Kuhn, H. H. Baer, and A. Gauhe, B. *88*, 1713 (1955)

Carboxylic acid amides from carboxylic acid esters $COOR \rightarrow CONH_2$
s. *6*, 435

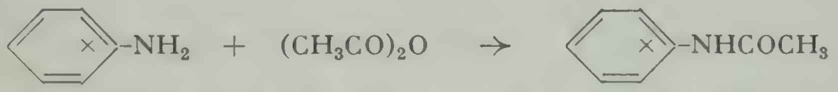
Hydrochlorides ←

Azomethines from amines and oxo compounds $CO + H_2N \rightarrow C{:}N$
s. *8*, 479

Quinone dioximes $CO \rightarrow C{:}NOH$
s. *7*, 117

Acylation of amines $NH \rightarrow NAc$

331.



Labeled compounds. Acetic anhydride added in 2 portions to aniline-1-C^{14} hydrochloride in CCl_4, refluxed 45 min. with stirring, after cooling methanol added to esterify excess acetic anhydride and acetic acid, methyl acetate slowly distilled off, then water removed by azeotropic distillation with CCl_4 introduced in several portions → acetanilide-1′-C^{14}. Y: ca. 100%.—The use of CCl_4 as a solvent avoids formation of diacetanilide. N. E. Searle and H. E. Cupery, J. Org. Chem. *19*, 1622 (1954).

Pyrazoles and isoxazoles from enolether acetals ○
s. *6*, 436

Purines from pyrimidines
Labeled compounds s. *8*, 481

Oxazolidines from 2-aminoalcohols
s. *9*, 471

Pyridine ring from 1,5-diketones
s. *8*, 480

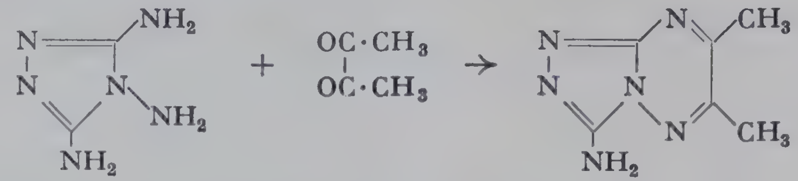
Pyridazine-3,6-diols from carboxylic acid anhydrides
s. *8*, 482; s. a. Am. Soc. *76*, 2201 (1954)

Pyrazine 1-oxides from aminonitriles and α-isonitrosoketones
s. *8*, 483

Hydrobromides ←

s-Triazolo[4,3-b]-as-triazines ←

332.

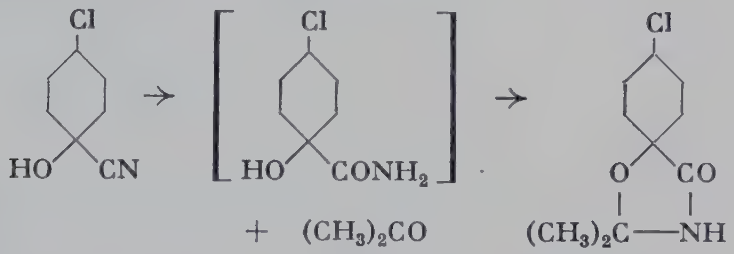


A soln. of guanazine hydrobromide and biacetyl in boiling water adjusted to pH 5 by careful addition of aq. NH_3, and kept overnight at 0° → 3-amino-6,7-dimethyl-*s*-triazolo[4,3-b]-*as*-triazine. Y: 83%. F. e. s. E. C. Taylor, Jr., W. H. Gumprecht, and R. F. Vance, Am. Soc. *76*, 619 (1954).

Halogen acids *HHal*

4-Oxazolidones from cyanohydrins via α-hydroxycarboxylic acid amides

333.



A cooled satd. soln. of HBr in acetic acid added at 10° to a mixture of *cis-* and *trans*-4-chlorocyclohexanone cyanohydrin, acetic acid, and some water, shaken 10 min. with ice-cooling until dissolved, shaking continued at room temp. for 1 hr., petroleum ether added, shaken 4 hrs., the crude product containing a little acid dissolved in acetone, and refluxed 1 hr. → *cis-* and *trans*-4-chloro-2′,2′-dimethyl-*spiro*-(cyclohexan-1,5′-oxazolidone). Y: 92%. F. e., also isolation of the intermediate, s. R. Grewe, W. Lorenzen, and L. Vining, B. *87*, 793 (1954); s. a. K. Eichenberger, E. Ganz, and J. Druey, Helv. *38*, 284 (1955).

Hydrofluoric acid/palladium-carbon *HF/Pd-C*
s. Palladium-carbon/hydrofluoric acid

Hydrochloric acid *HCl*

Glycosamines OH → NHR
s. *8*, 484

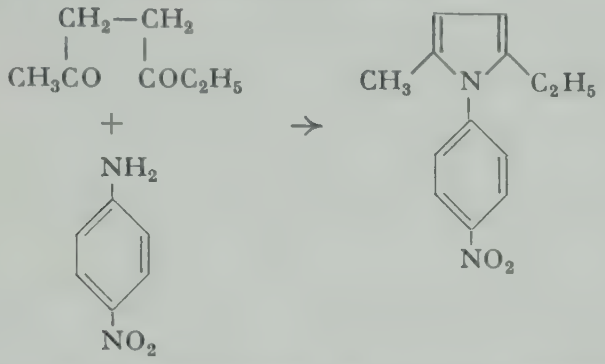
Aminodesoxybenzoins from benzoins ←
Voigt reaction
s. *9*, 472

1,1-Di(acylamino) compounds from 1-alkoxy-1-acylamines C(OR)NHAc → $C(NHAc)_2$
s. *8*, 485

Thiosemicarbazones from aldehydes $CHO \rightarrow CH{:}NNHCSNH_2$
s. *7*, 262

Characterization of γ-diketones by formation of 1-(p-nitrophenyl)pyrroles ○

334.

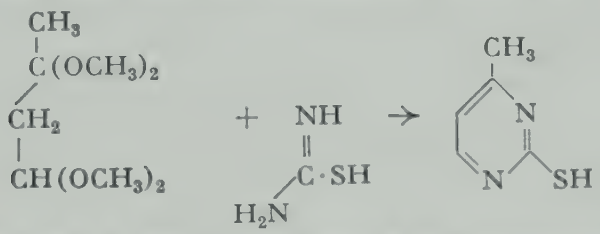


Heptane-2,5-dione and p-nitraniline in alcohol containing 1 drop of concd. HCl refluxed 3 hrs. → 1-(p-nitrophenyl)-2-methyl-5-ethylpyrrole. Y: 92%. F. e. s. M. Fétizon and P. Baranger, C. r. *236*, 1428 (1953).

2-Thiohydantoins
s. *8*, 486

N-Heterocyclics from acetoacetaldehyde bisacetal

35.



Concd. HCl added to a soln. of thiourea and acetoacetaldehyde bis(dimethylacetal) in ethanol, and the product isolated after several hrs. → 2-mercapto-4-methylpyrimidine. Y: almost 100%. F. e. s. W. Franke and R. Kraft, B. *86*, 797 (1953).

Imidazole ring – Phillips reaction
s. *4*, 398; s. a. J. R. E. Hoover and A. R. Day, Am. Soc. *77*, 4324 (1955)

2,4-Diazafluoranthenes
s. *6*, 437

Phenoxazine ring
s. *9*, 473

Nickel *Ni*

Prim. amines from aldehydes $CHO \rightarrow CH_2NH_2$
s. *5*, 313; limitation by formation of carbinols s. M. Métayer and Ng. Dat-Xuong, Bl. *1954*, 615

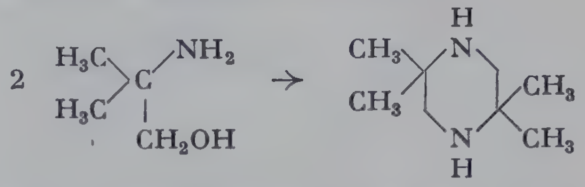
Prim. amines from α-ketoaldehydes via α-sec-aminoketones ←
s. *8*, 487

Sec. from prim. amines and alcohols $NH_2 \rightarrow NH$
s. *10*, 337

Sec. amines from aldehydes $CHO \rightarrow CH_2NH$
Carbohydrate derivatives s. *8*, 488

Cyclodehydration
Piperazines from 2 2-aminoalcohol molecules

336.

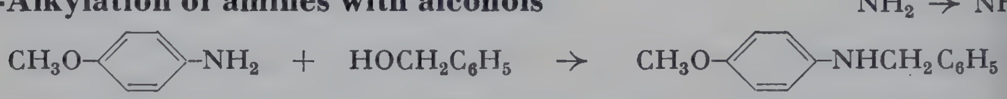


2-Amino-2-methyl-1-propanol heated 8 hrs. with Raney-Ni at 250° an an initial H_2-pressure of 2700-3000 p. s. i. → 2,2,5,5-tetramethylpiperazine. Y: 50-63%. S. M. McElvain and L. W. Bannister, Am. Soc. 76 1126 (1954).

Nickel-silica/potassium benzoxide *Ni-SiO_2/KO*

N-Alkylation of amines with alcohols $NH_2 \rightarrow NH$

337.



Aceotropic water entrainment. 0.125 mole p-methoxyaniline in xylene, 1 g U.O.P.-nickel, and boiling chips added to a soln. of 0.04 mole K in 0.2 mole benzyl alcohol, and vigorously refluxed with separation of th water formed, refluxing continued for at least 2 hrs. after water separation has stopped, and the product isolated as the hydrochloride → N-benzyl-p-methoxyaniline hydrochloride. Y: 93%.—Similarly: n Decanol and aniline → N-n-decylaniline. Y: 76%. F. e. s. E. F. Prat and E. J. Frazza, Am. Soc. *76*, 6174 (1954); with Raney-Ni s. R. G. Ric and E. J. Kohn, Am. Soc. *77*, 4052 (1955).

Palladium-barium sulfate/aluminum chloride *Pd-$BaSO_4$/$AlCl$*

Tert. from prim. and sec. amines $NH \rightarrow N$
s. *6*, 438

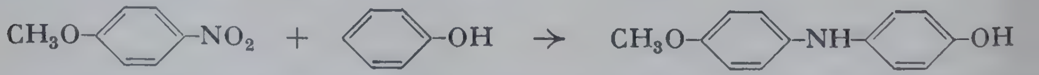
Palladium-carbon *Pd-*

Sec. and tert. amines from
prim. amines or nitro compounds and aldehydes
Alkylaminocarboxylic acids
Methylation of amines
s. *7*, 459

Palladium-carbon/hydrofluoric acid *Pd-C/H*

Reductive substitution ←
Sec. amines from nitro compounds

338.



A mixture of p-nitroanisole, phenol, 3%-Pd-on-carbon, and HF hydrogenated 2 hrs. at 40-45° and 13-20 atm. → 4-hydroxy-4′-methoxydiphe nylamine. Y: ca. 100% based on startg. m. consumed; conversion 66%. F. e. s. V. Weinmayr, Am. Soc. 77, 1762 (1955).

Platinum oxide *PtO_2*

Methylation of amines $NH_2 \rightarrow N(CH_3)_2$
s. *7*, 460

Sec. from prim. amines and oxo compounds $NH \rightarrow NR$
Aminoalcohols s. *6*, 439

2-Pyrrolidones from γ-ketocarboxylic acids ○
s. *6*, 440

Via intermediates *v.i.*

Amines from carboxylic acids
via carboxylic acid chlorides and amides $COOH \rightarrow CH_2N\langle$
s. *6*, 461; steroid amines s. H. L. Herzog, C. C. Payne, and E. B. Hershberg, Am. Soc. *77*, 5324 (1955)

Subst. carboxylic acid amides
from carboxylic acids via carboxylic acid chlorides $COOH \rightarrow CON\langle$
s. *9*, 627

Mixed and partial dicarboxylic acid derivatives
Avoidance of isomerization
s. *9*, 474

Peptide synthesis with chlorophosphites
s. *9*, 475; s. a. D. T. Elmore and P. A. Toseland, Soc. *1954*, 4533

Carboxylic acid hydrazides from carboxylic acids $COOH \rightarrow CONHNH_2$
via carboxylic acid esters
s. *9*, 476

via carboxylic acid chlorides
s. *9*, 503

Hydantoins from α-isocyanatocarboxylic acid esters ○
s. *9*, 477

Tetrazoles from carboxylic acid amides via iminochlorides
s. *6*, 441

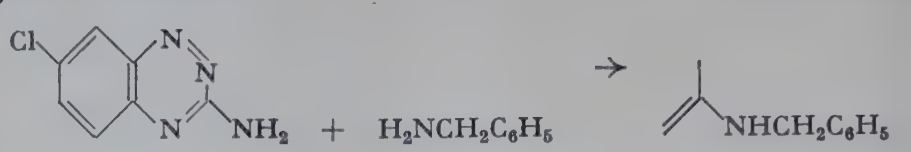
Nitrogen ↑ NC N

Without additional reagents *w.a.r.*

Sec. from prim. amines $NH_2 \rightarrow NHR$
Exchange of substituents of pyrimido[4,5-b]pyrazines
s. *9*, 534

Benzylation of amines $NH \rightarrow NCH_2C_6$

339.



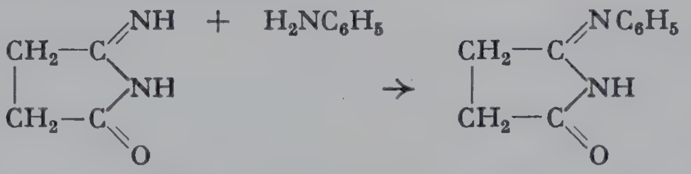
7-Chloro-3-amino-1,2,4-benzotriazine refluxed with benzylamine →
chloro-3-benzylamino-1,2,4-benzotriazine. Y: 78%.—The reaction do
not proceed with common alkyl amines and ar. amines. F. J. Wolf
al., Am. Soc. *76*, 4611 (1954).

Sec. and tert. amines from
quaternary ammonium salts by transamination $NH \rightarrow N$
s. *9*, 478

Betaines from aminocarboxylic and aminosulfonic acids
and from peptides
s. *7*, 462

Substitution of imino groups $:NH \rightarrow :N$

340.



0.33 g. 5-imino-2-pyrrolidone and 0.5 cc. aniline in 2-methoxyethan
boiled 3 hrs. → 0.5 g. 5-phenylimino-2-pyrrolidone. J. A. Elvidge ar
R. P. Linstead, Soc. *1954*, 442.

4-Pyridones from 4-nitropyridines
s. *7*, 463

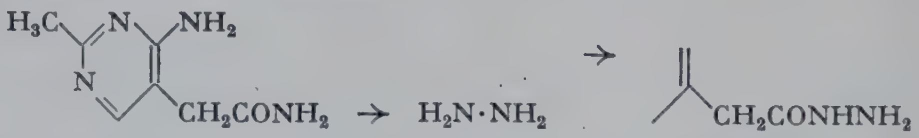
Substitution of carboxylic acid amides $CONH_2 \rightarrow CONH$
s. *9*, 479

Acylaminoalcohols from aminoalcohols $NH \rightarrow N$
Selective N-acylation
s. *7*, 423

Replacement of amino by hydrazino groups $NH_2 \rightarrow NHN$
s. *8*, 489

Carboxylic acid hydrazides $CONH_2 \rightarrow CONHN$
from carboxylic acid amides

341.



4-Amino-2-methyl-5-pyrimidylacetamide heated 30 min. at 100° wi
100%-hydrazine hydrate → 4-amino-2-methyl-5-pyrimidylacethydr
zide. Y: 89%. F. e., also aminocarboxylic acid hydrazides from la
tams, s. P. Nesbitt and P. Sykes, Soc. *1954*, 3057.

Replacement of mobile nitro groups by hydrazino groups $NO_2 \rightarrow NHNH_2$
s. *6*, 442

Substitution of carboxylic acid thioamides $CSNH_2 \rightarrow CSNHR$
Dithioöxamides s. *9*, 480

Ureas from amines $NH_2 \rightarrow NHCONH_2$

and N-nitrosoureas
s. *8*, 490

and carboxylic acid azides $NH_2 \rightarrow NHCONHR$
s. *9*, 481

Sym. ureas $OC(NHR)_2$
s. *7*, 464; from monosubst. ureas s. *6*, 443

Semicarbazides from ureas $NHCONH_2 \rightarrow NHCONHNH_2$
s. *9*, 482

Cleavage of N-thioacylamidines ←
Diamidides s. *9*, 483

Amine salts of N-nitramines from N-nitrourethans ←
s. *9*, 484

Imidazolidones from ureas ○
s. *7*, 465

4-Subst. 2-acylimidazoles from α-halogenoketones via α-azidoketones
s. *9*, 485

Imidazole ring from carboxylic acid amides
Bi(benzimidazoles) s. *9*, 486

Oxazolines from α-aminoalcohols
s. *8*, 491

2-Oxazolidones from α-aminoalcohols and urea
s. *7*, 466

Copazolines
s. *9*, 487

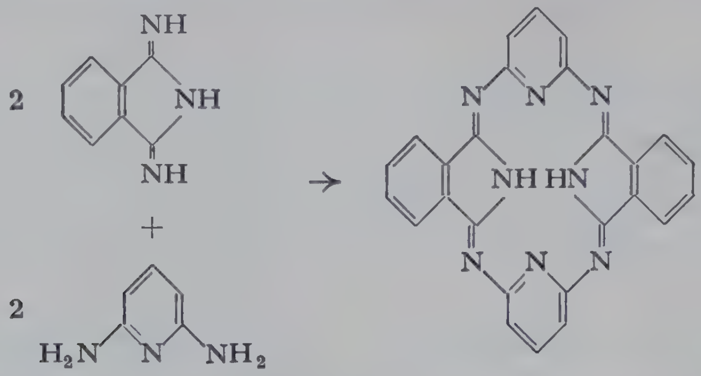
Pyrimido[4,5-b]pyrazines from pyrazines
s. *9*, 488

Benzo-1,2,4-thiadiazine 1,1-dioxides
s. *6*, 467

One-step purine synthesis
s. *7*, 516

Conjugated N-macrocyclics from imidines

342.



6 g. 1,3-Diiminoisoindoline and 4.6 g. 2,6-diaminopyridine refluxed hrs. in n-butanol → 3.5 g. macrocycle. J. A. Elvidge and R. P. Linstead, Soc. *1952*, 5008; *1954*, 2490.

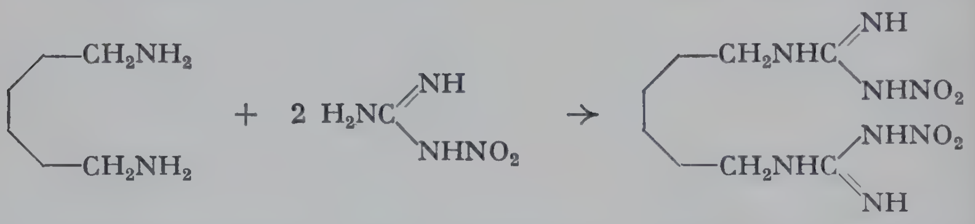
Sodium hydroxide *NaOH*

Hydroxylamines from quaternary ammonium salts ←
s. *9*, 553

Potassium hydroxide *KOH*

Subst. nitroguanidines NH_2 → NHC(:NH)NHNO

343.



Aq. hexamethylenediamine dihydrochloride added with stirring at 40 to a soln. of 2 moles nitroguanidine in aq. KOH, and allowed to stand for 2 hrs. → 1,6-bis(nitroguanidino)hexane. Y: 84.8%. C. M. Samour and J. P. Mason, Am. Soc. *76*, 441 (1954); cf. Synth. Meth. *4*, 415.

Potassium hydroxide/alcohol

Replacement of nitro groups ←
s. *9*, 491

Sodium/alcohol *NaO*

Selective N-alkylation NH → N
s. *9*, 489

Phenyllithium *C_6H_5L*

Diazo compounds from sulfonic acid azides CH_2 → CN
s. *9*, 490

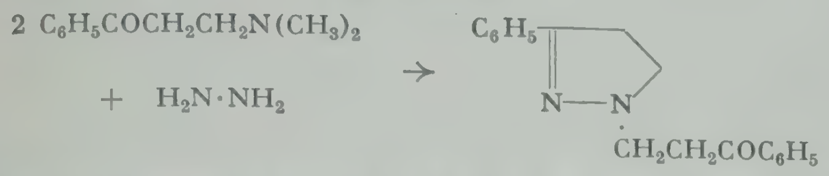
Sodium carbonate *Na_2CO_3*

N-Amino-N′-nitroguanidines from N-nitroso-N′-nitroguanidines ←
s. *8*, 492

Sodium hydrogen carbonate *$NaHCO_3$*

Pyrazolines from
2 β-aminoketone molecules and hydrazine ○

344.



85%-Hydrazine hydrate added to a soln. of β-dimethylaminopropiophenone hydrochloride in satd. aq. $NaHCO_3$, and refluxed 45 min. on a steam bath → 1-(β-benzoylethyl)-3-phenyl-Δ^2-pyrazoline (startg. m. f. 640). Y: 83.4%. M. Stamper and B. F. Aycock, Am. Soc. *76*, 2786 (1954).

Potassium carbonate *K_2CO_3*

Sec. from prim. amines and nitro compounds $NO_2 \rightarrow NHR$
s. *8*, 493

Replacement of nitro groups ←
Partial replacement by amino groups
s. *9*, 491

Potassium hydrogen carbonate *$KHCO_3$*

Nitrones from pyridinium salts C:N(O)R
s. 7, 468; s. a. W. J. Leanza et al., Am. Soc. *76*, 1691 (1954)

Sodium nitrite *$NaNO_2$*

3-Nitrosoöxazolidines from 2 2-aminoalcohol molecules ○
s. *9*, 492

Copper *Cu*

α-Aminoketones from α-diazoketones $COCHN_2 \rightarrow COCH_2N<$
s. *9*, 493

Silver carbonate *Ag_2CO_3*

Substitution of amidines NH → NR
s. *9*, 494

Silver nitrate *$AgNO_3$*

Azomethines from azo compounds CHN:NR → C:NR′
s. *6*, 444

Zinc *Zn*

Formamides from azo compounds ·N:NR → ·NHCHO
s. *6*, 519

Imidazolecarboxamidines from ←
malondiamidines via azomalondiamidines
s. 7, 469

Alumina Al_2O_3
Selfcondensation $2\,RNH_2 \rightarrow R_2NH$
s. *6*, 445

Aluminum chloride $AlCl_3$
Azines from hydrazones $2\,R_2C{:}NNH_2 \rightarrow R_2C{:}N{\cdot}N{:}CR_2$
s. *9*, 495

Phenol C_6H_5OH
Prim. amines from quaternary ammonium salts ←
s. *8*, 494

Acetic acid CH_3COOH
Transosazonation ←
s. *6*, 447

Formylhydrazines NHNHCHO
s. *7*, 470

Pyrazoles from ethyleniminoketones ○
s. *9*, 496

Sulfonic acid chlorides RSO_2Cl
Diglycosamines from glycosamines $2\,RNH_2 \rightarrow R_2NH$
s. *7*, 471

Sulfonates ←
N-Cyanoethylation by amine exchange $NH_2 \rightarrow NHCH_2CH_2CN$
s. *8*, 495

Subst. guanidines from cyanoguanidines ←
s. *8*, 399

Imidazolines and other 1,3-diazacycloalkenes from subst. amidines ○
s. *6*, 448

Δ^2-Oxazolines from 2-aminoalcohols
s. *6*, 449

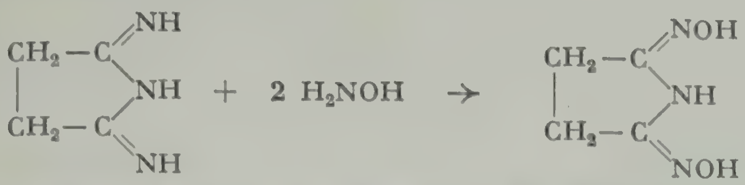
Sulfate ←
Labeled purines by transformylation
s. *9*, 497

Sulfuric acid H_2SO_4
Azines from ketones via hydrazones ←
s. *6*, 450

Hydrochlorides ←
Substitution of carboxylic acid amides CONH → CONR
s. *10*, 296; also substitution of dicarboxylic acid imides s. D. Klamann, M. *84*, 925 (1953)

Hydroxylimines from imines ←

345.



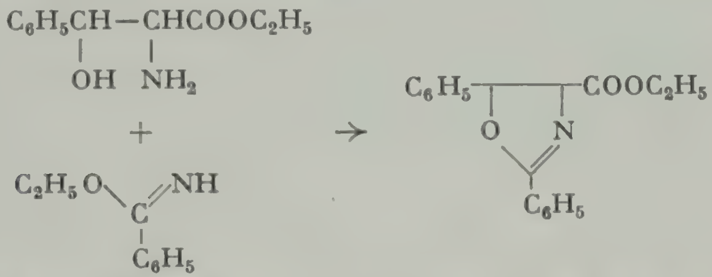
0.5 g. succinimidine (prepn. s. 269) and 1 g. hydroxylamine hydrochloride in ethanol refluxed 2.5 hrs. → 0.5 g. 2,5-dihydroxyiminopyrrolidine. F. e. s. J. A. Elvidge and R. P. Linstead, Soc. *1954*, 442.

Subst. oxamidines ←
s. *6*, 451

Imidazole ring from iminoesters ○
s. *6*, 452

Oxazolines from 2-aminoalcohols
Masking of 2-aminohydroxy groups

346.



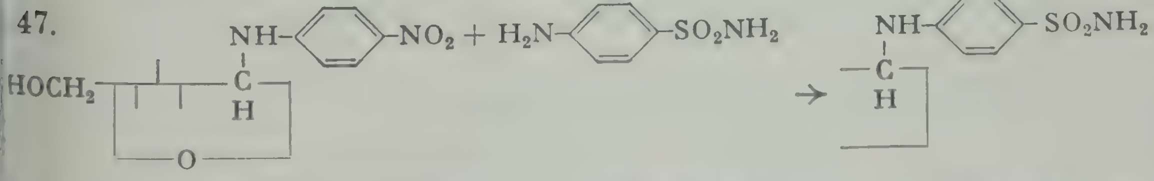
An intimate mixture of *allo*-DL-phenylserine ethyl ester and benzimido ethyl ester hydrochloride heated slowly to 100° on a water bath, and the product isolated after 20 min. → ethyl *erythro*-DL-2,5-diphenyloxazoline-4-carboxylate. Y: 76%. M. Viscontini and E. Fuchs, Helv. *36*, 1 (1953).

Purines from imidazoles
s. *7*, 472

Hydrochloric acid *HCl*

Transamination of glycosamines NR → NR′

47.



p-Nitranilineglucoside allowed to react with sulfanilamide in abs. alcohol containing abs. HCl → sulfanilamide N^4-glucoside. Y: 97%. F. e. s. R. Bognár and P. Nánási, Nature *171*, 475 (1953); Soc. *1955*, 193.

Ureas from amines $NH_2 \rightarrow NHCONH_2$
s. *7*, 473

Benzimidazole derivatives in identification of carbohydrates ○
s. *9*, 498

Oxazolone ring opening with dimerization C
s. *9*, 499

Palladium-barium sulfate *Pd-BaSO$_4$*

Tert. amines from nitriles CN → CH_2NR_2
s. *7*, 474

Platinum oxide *PtO$_2$*

Reductions of α-diazoketones ←
α-Aminoalcohols from α-diazoketones
s. *7*, 475

Via intermediates *v.i*

Subst. carboxylic acid amides $CONHNH_2$ → CONHR
from carboxylic acid hydrazides
via carboxylic acid azides
s. *6*, 226; s. a. M. Brenner and K. Rüfenacht, Helv. *36*, 1832 (1953)

Peptide synthesis
s. *7*, 476/7; s. a. N. C. Davis and E. L. Smith, Biochem. Prep. *4*, 38 (1955); oxytocin synthesis s. R. A. Boissonnas et al., Helv. *38*, 1491 (1955)

Halogen ↑ NC⇅Hal

Without additional reagents *w.a.r.*

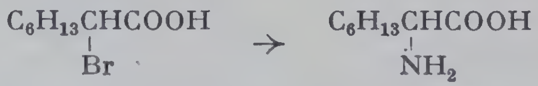
Prim. amines from halides Hal → NH_2
Aminoacetals
s. *3*, 359; s. a. R. B. Woodward and W. E. Doering, Org. Synth., Coll. Vol. III, 50 (1955)

Replacement of halogen by amino groups
Sulfonic acids as intermediates
Nitration with simultaneous sulfonation
Desulfonation
s. *7*, 478

Replacement, also partial, of chlorine by amino groups Cl → NH_2
s. *10*, 390

α-Aminocarboxylic acids from α-bromocarboxylic acids Br → NH_2

348.



$$C_6H_{13}\underset{Br}{CH}COOH \rightarrow C_6H_{13}\underset{NH_2}{CH}COOH$$

α-Bromocaprylic acid in abs. alcohol satd. at 0° with NH_3 allowed to stand 3 days at room temp. → α-aminocaprylic acid. Y: 95%. F. e. s. S. M. Birnbaum, Shou-Cheng J. Fu, and J. P. Greenstein, J. Biol. Chem. *203*, 333 (1953).

Sec. from prim. amines and halides
s. *6*, 453; *9*, 930

$\text{Hal} \rightarrow \text{NHR}$

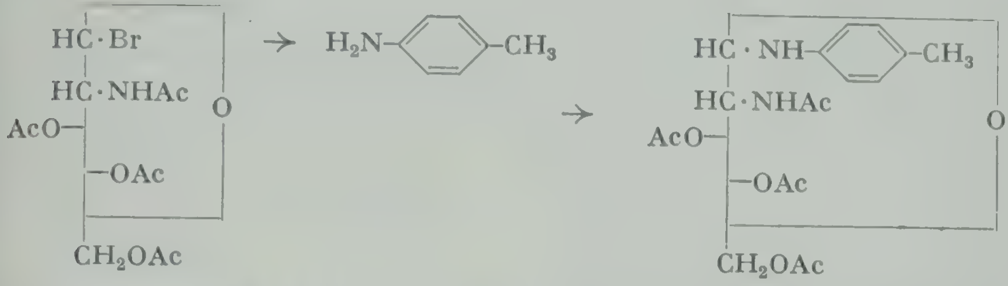
Tert. amines from halides
Simple method s. *7*, 479

$3\,\text{RHal} \rightarrow R_3N$

Glycosaminides

$\text{Hal} \rightarrow \text{N}\langle$

49.



A soln. of bromo-2.3,4,6-tetraacetyl-ᴅ-glucosamine in chloroform mixed with a soln. of p-toluidine in the same solvent, and allowed to stand 1 day at 20° → 2.3,4,6-tetraacetyl-ᴅ-glucosamine-p-toluidide. Y: 82.2%. F. e. s. A. Bertho and D. Koziollek, B. 87, 934 (1954).

Aminolactones from halogenolactones
s. *7*, 480

Exchange of substituents of pyrimidines
s. *9*, 500

Partial replacement of halogen by amino groups
s. *8*, 497

  Halogenamines from dihalides
  s. *8*, 496

  Replacement of chlorine in pyrimidines
  s. *8*, 498

  1,3,5-Triazine derivatives
  s. *8*, 499

Tert. from sec. amines

$R_2NH \rightarrow R_2NR'$

  Allyl rearrangement
  s. *7*, 481

  Aminoalcohols from halogenhydrins
  s. *7*, 482

Aminoalcohols from acoxyhalides
s. *7*, 483

←

Replacement of bromine by nitro groups with simultaneous formation of sulfoxides from thioethers
s. *8*, 500

←

Enamines from 1,2-dibromides $CHBrCHBr \rightarrow CH{:}C{\cdot}N<$
s. *6*, 454

2-Ethyleneamines from β,γ-ethylenehalides with subsequent N-acylation ←
s. *9*, 501

Carboxylic acid amides from carboxylic acid chlorides $COCl \rightarrow CONH_2$

Lower aliphatic amides
s. *9*, 502

Optically active compounds
s. *7*, 484

Subst. carboxylic acid amides from carboxylic acid chlorides $COCl \rightarrow CON<$
s. *8*, 501; *9*, 474

Sulfocarboxylic acid derivatives
s. *8*, 502

α-Chlorocarboxylic acid amides from α-chlorocarboxylic acid chlorides
s. *8*, 934

Dicarboxylic acid amide esters from dicarboxylic acid chloride esters $COCl \rightarrow CONH_2$

350. $C_2H_5OOC[CH_2]_4COCl \rightarrow C_2H_5OOC[CH_2]_4CONH_2$

Dry NH_3 bubbled through a soln. of crude 5-carbethoxyvaleryl chloride in dioxane for 30 min. with ice-cooling, and the NH_3-flow continued for 30 min. after removal of the ice-bath → ethyl adipamate. Y: 75%.—Ethyl perfluoroadipamate (cf. 173) could not be prepared in tis manner because of the increased reactivity of the ester group. W. H. Rauscher and H. Tucker, Am. Soc. *76*, 3599 (1954).

Carboxylic acid hydrazides from carboxylic acids via carboxylic acid chlorides $COCl \rightarrow CONHNH_2$
s. *9*, 503

Subst. carboxylic acid hydrazides from carboxylic acid chlorides $COCl \rightarrow CONHNHR$
s. *8*, 503

Carboxylic acid carbobenzoxyhydrazides $COCl \rightarrow CONHNHCOOR$
s. *9*, 504

1-Subst. iminopyridones
s. *10*, 584

Isocyanates from amines via carbamyl chlorides $NH_2 \rightarrow N{:}C{:}O$
s. *6*, 455

Di-isocyanates from diamines
s. *6*, 456

Urethans from chloroformates $ROCOCl \rightarrow ROCONH_2$
s. *7*, 300

Cyanamides from amines

NH → N·CN

s. *10*, 270

Ureas from amines via cyanamides

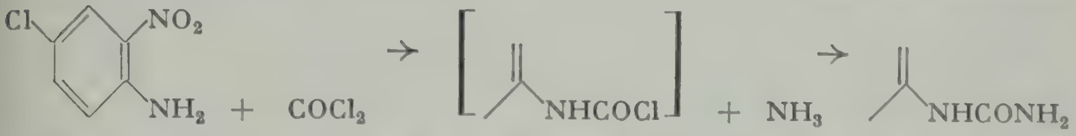
51. $C_6H_5CH_2NH_2 + BrCN \rightarrow [C_6H_5CH_2NHCN] \rightarrow C_6H_5CH_2NHCONH_2$

An ethereal soln. of cyanogen bromide added dropwise with stirring and ice-water cooling to an ethereal soln. of 2 mole benzylamine, the benzylamine hydrobromide precipitate removed by filtration, the filtrate extracted with 5 mole aq. KOH, and heated 3 hrs. on a steam bath → benzylurea. Y: 68%. F. e. s. W. L. Garbrecht and R. M. Herbst, J. Org. Chem. *18*, 1014 (1953).

Monosubst. ureas from amines

$NH_2 \rightarrow NHCONH_2$

52.

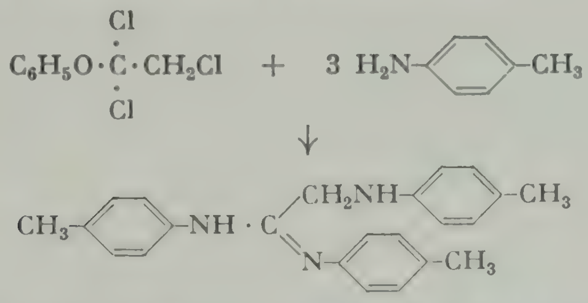


Excess phosgene passed at 60° into a suspension of 4-chloro-2-nitroaniline during 5 hrs., allowed to stand overnight at room temp., part of the solvent distilled off in vacuo, then anhydrous NH_3 added over a period of 45 min. at such a rate that the temp. remains below 20° until no more yellow precipitate forms → 4-chloro-2-nitrophenylurea (startg. m. f. 256). Y: 80%. F. J. Wolf et al., Am. Soc. *76*, 4611 (1954).

Sabaneyev bases from 1-alkoxy-1,1,2-trihalides

←

3.



A mixture of α,α,β-trichloroethyl phenyl ether and p-toluidine warmed 35 min. at 50-60° → N-(p-tolyl)glycine-N,N′-di-(p-tolyl)amidine. Y: 50%. F. e. s. E. Ziegler, W. Kaufmann, and W. Klementschitz, M. *83*, 1334 (1952).

S-Thiocarbamic acid esters from amines and thiocarbonyl chloride

$NH_2 \rightarrow NHCOSR$

s. *9*, 536; s. a. R. Riemschneider and A. Kühl, M. *84*, 1238 (1953)

Sulfonic acid hydrazides from chlorides

$Cl \rightarrow NHNHSO_2R$

s. *6*, 121

Sym. thioureas from amines

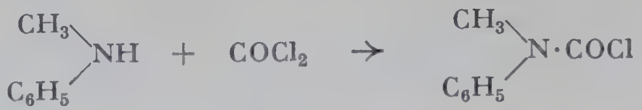
$2\,RNH_2 \rightarrow (RNH)_2CS$

s. *9*, 505

Carbamyl chlorides from amines

NH → NCOCl

354.



A soln. of N-methylaniline in ethyl acetate added dropwise during 1.5-2 hrs. to ethyl acetate satd. with phosgene while a vigorous stream of phosgene is introduced, then warmed cautiously in a water bath, finally the solvent removed by distillation → N-methyl-N-phenylcarbamyl chloride (start. m. f. 629). Y: 75-85%. F. Weygand and R. Mitgau, B. *88*, 301 (1955).

s. a. *6*, 455

Cyclic imines from dibromides

○

s. *7*, 485

Pyrrolines
s. *7*, 486

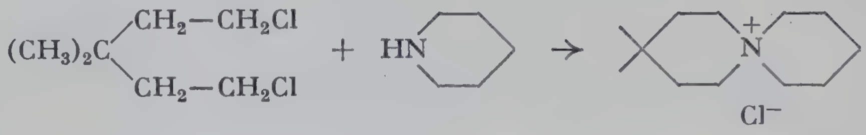
3-Spirocyclopropane-Δ^1-pyrrolines
s. *7*, 487

Azepine ring

s. *8*, 504

N-spiro-Ammonium salts

355.

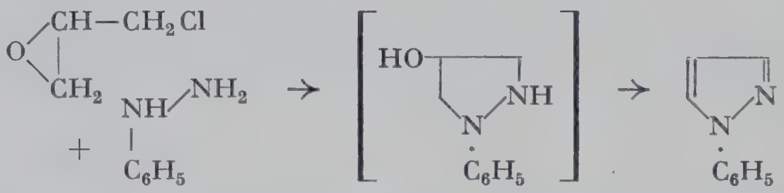


A mixture of piperidine and 1,5-dichloro-3,3-dimethylpentane (prepn. s. 544) heated to 110°, and the product isolated after ca. 10 min. → 4,4-dimethylbispiperidinium chloride. Y: 80%. L. Schmerling and J. P. West, Am. Soc. *74*, 2885 (1952).

s. a. *8*, 505

Pyrazoles

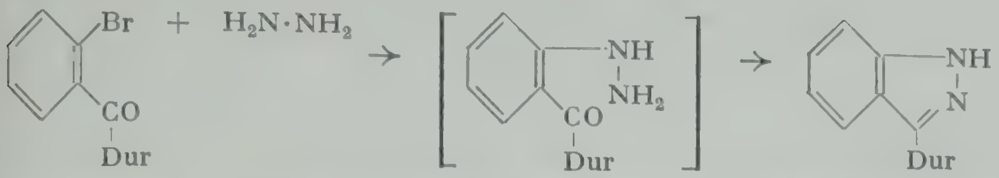
356.



95 g. phenylhydrazine added to 40 g. epichlorohydrin in 60%-ethanol, warmed cautiously on a steam bath to start a reaction which is then moderated by cooling, when the vigorous reaction subsides refluxed 1 hr., the solvent evaporated, the residue heated at 170° until after ca. 30 min. another vigorous reaction sets in, and after this reaction subsides heated to 200° for 10 min. → 44.9 g. 1-phenylpyrazole (Y: 72%) and 32 g. aniline. F. e. s. I. L. Finar und K. E. Godfrey, Soc *1954*, 2293.

Isoindazoles

357.



A mixture of o-bromobenzoyldurene, 85%-hydrazine hydrate, and 1-butanol refluxed 38 hrs. → 3-durylisoindazole. Y: 95%. R. C. Fuson and W. C. Hammann, Am. Soc. *74*, 1626 (1952).

Cycl. guanidines from halogenocyanamides

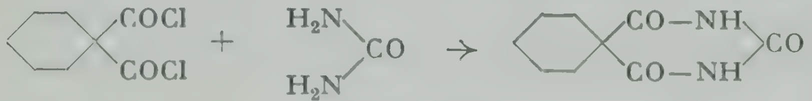
s. *6*, 458

Imidazolines from carboxylic acid amides via iminochlorides and amidines

s. *6*, 457

Barbituric acid derivatives from α-dicarboxylic acid chlorides

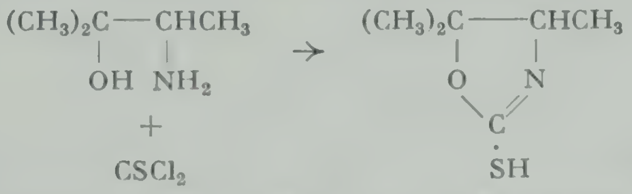
58.



A mixture of cyclohexane-1,1-dicarboxylic acid chloride (prepn. s. 634) and urea heated cautiously → cyclohexane-1,5-spiro-2,4,6-trioxohexahydropyrimidine. Y: 75%. F. e. s. G. Kühnhanss and J. Teubel, J. pr. *1*, 87 (1955).

Oxazolines from 2-aminoalcohols and thiophosgene

9.



Thiocarbonyl chloride added at 0° to a soln. of 2-amino-3-methylbutan-3-ol in benzene → 2-mercapto-4,5,5-trimethyl-2-oxazoline. Y: 95%. E. D. Bergmann and D. F. Herman, J. Appl. Chem. *3*, 42 (1953).

Pyrimidazoles

s. *6*, 459

6,7,8,9-Tetrahydropyrido[1,2-a]benzimidazoles

s. *8*, 506

2,5-Oxazolidiones

s. *8*, 507; from α-aminocarboxylic acids s. *6*, 461

1,3,4-Oxadiazolones

s. *6*, 460; in aq. soln. s. A. Stempel, J. Zelauskas, and J. A. Aeschlimann, J. Org. Chem. *20*, 412 (1955)

Lithium *Li*

Tert from sec. amines with meta-rearrangement $R_2NH \rightarrow R_2NR'$
s. 7, 488

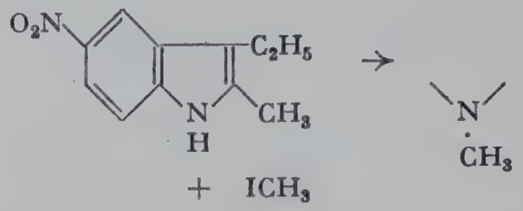
Sodium *Na*

N-Subst. 2-oxazolidones – Carbamyl derivatives $N \cdot CONH_2$
s. 7, 489

Sodium hydride *NaH*

N-Alkylation $NH \rightarrow NR$

360.

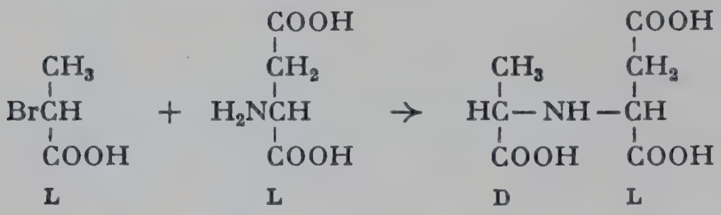


2-Methyl-3-ethyl-5-nitroindole allowed to react with NaH in toluene-*dimethylformamide* under N_2, methyl iodide added to the resulting Na-salt, warmed to ca. 60°, and the product isolated after 4 hrs. → 1,2-dimethyl-3-ethyl-5-nitroindole. Y: 77%. E. Shaw, Am. Soc. *76*, 1384 (1954).

Sodium hydroxide *NaOH*

Sec. from prim. amines and halides $Hal \rightarrow NHR$

361.



$$\underset{\text{L}}{CH_3CHBrCOOH} + \underset{\text{L}}{HOOCCH_2CH(NH_2)COOH} \rightarrow \underset{\text{D}}{CH_3CH(COOH)}-NH-\underset{\text{L}}{CH(COOH)CH_2COOH}$$

Walden inversion. A soln. of L-α-bromopropionic acid and L-aspartic acid in aq. NaOH kept 6 days at 37°, then chromatographed with Amberlite IR-100 which absorbs Na^+ and amino acids more strongly than imino acids → α-(D-1-carboxyethylamino)-L-succinic acid. Y: 66%.— Walden inversion takes place during the synthesis. F. e. and stereoisomers with lower yields s. F. Kögl, J. de Flines, and D. H. W. den Boer, R. *72*, 1009 (1953).

Acylation of aminocarboxylic acids $NH \rightarrow NAc$
s. *9*, 501

Selective N-acylation of aminohydroxycarboxylic acids
s. *9*, 506

N-Carbalkoxy derivatives from amines $NH \rightarrow NCOOR$
s. *7*, 366, 490; s. a. N. C. Davis and E. L. Smith, Biochem. Prep. *4*, 38 (1955)

Selective N-carbalkoxylation
s. *9*, 507

Blocking of α-aminocarboxylic acid groups
s. *7*, 490

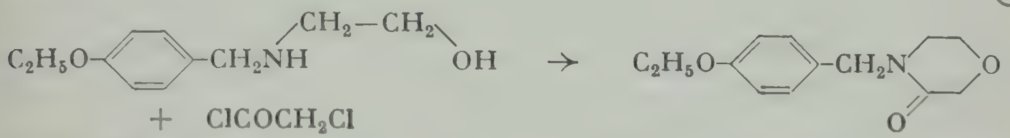
Carbalkoxycyanamides
s. *9*, 508

Sym. ureas from amines and phosgene $CO(NHR)_2$
s. *8*, 508

Sulfonylureas from sulfonylisoureas ←
s. *7*, 58

3-Morpholones ○

62.



35%-NaOH added to a soln. of 1 mole N-(4-ethoxybenzyl)ethanolamine in 50%-ethanol, then 2.5 moles chloroacetyl chloride added simultaneously with more 35%-NaOH during ca. 1 hr. with vigorous stirring and ice-cooling at 15-20°, stirring continued 30 min. at ca. 20° → N-(4-ethoxybenzyl)-3-morpholone. Y: 81%. F. e., also 2-step procedure, s. A. R. Surrey et al., Am. Soc. 77, 633 (1955).

Phenoxazines
s. *9*, 509

Potassium hydroxide *KOH*

Betaines from aminocarboxylic acids ←
s. *9*, 510

Acyldicyanodiamides NH → NAc
s. *9*, 511

2-Oxazolidones from 2-aminoalcohols and phosgene ○
s. *8*, 509

Potassium hydroxide/acetone

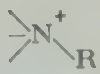
Selective N-alkylation NH → NR
Substitution of carboxylic acid amides
s. *9*, 512

Sodium/alcohol *NaOR*

Alkoximes from isomeric oximes ←
s. *6*, 462

Carbethoxy derivatives of amines NHCOOR
s. *6*, 463

Quaternary ammonium salts

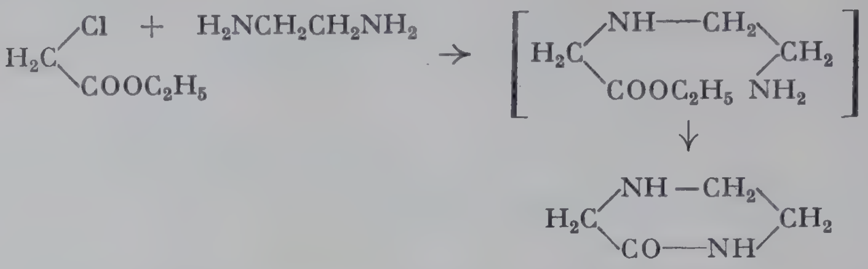


s. *8*, 343

Ring closure due to steric hindrance ○
s. *9*, 513

Piperazinones

363.

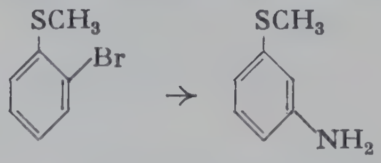


A soln. of ethyl chloroacetate in abs. alcohol added at room temp. during ca. 3 hrs. to a well-stirred soln. of anhydrous ethylenediamine in abs. alcohol, allowed to stand for 2 hrs., a soln. of Na in alcohol added, the precipitated NaCl filtered off, alcohol and excess ethylenediamine removed by distillation at the water pump, and the residue distilled at 200°/5 mm. bath temp. → 2-piperazinone. Y: 45%. F. e. s. S. R. Aspinall, Am. Soc. *62*, 1202 (1940); s. a. R. L. Hodgson, I. R. C. Bick, and D. J. Cram, Am. Soc. *76*, 1137 (1954).

Alkali amides ←

Replacement of halogen by amino groups with position shift of substituents of isocyclics ←

364.



o-Bromophenyl methyl sulfide added during 10 min. to a soln. of $NaNH_2$ in liq. NH_3, and stirring continued for 10 min. → m-aminophenyl methyl sulfide. Y: 57.5% based on startg. m. consumed. Also reaction of the chloro analog with KNH_2 s. H. Gilman and G. A. Martin, Am. Soc. *74*, 5317 (1952).

s. a. *9*, 539

Lithium amide *$LiNH_2$*

N-Alkylation NH → NR

Substitution of carboxylic acid amides

s. *9*, 514

Sodium amide *$NaNH_2$*

α,β-Acetylene-prim-amines from α,β-acetylenechlorides Cl → NH_2

s. *9*, 515

N-Alkylation NH → NR

s. *9*, 539; s. a. W. Schindler and F. Häfliger, Helv. *37*, 472 (1954)

Acylamines from halides Hal → NHCOR

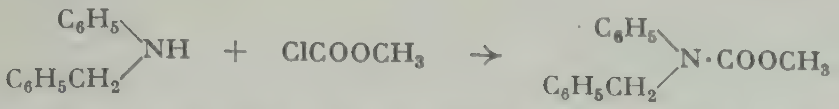
Substitution of carboxylic acid amides

s. *8*, 510

Urethans from amines

NH → NCOOR

365.



A soln. of benzylaniline in anhydrous toluene added to $NaNH_2$ in toluene, refluxed 3 hrs. with stirring, methyl chloroformate in toluene added, and refluxed 4 hrs. with stirring → methyl N-phenyl-N-benzylcarbamate. Y: 76%. J. H. Biel et al., Am. Soc. 77, 2250 (1955).

Sodium carbonate

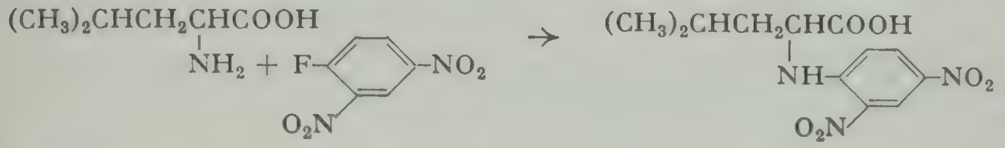
Na_2CO_3

Sec. from prim. amines and fluorides

2,4-Dinitrophenyl derivatives of amines

F → NHR

366.



Simplified procedure. L-Leucine and Na-carbonate dissolved in water at 40°, 1 molar equivalent of 1-fluoro-2,4-dinitrobenzene added, and vigorously stirred at ca. 40° for 30 min. → N-2,4-dinitrophenyl-L-leucine. Y: 97%.—By the above procedure, a more rapid reaction can be achieved, ethanol evaporation and extraction of excess reagent can be eliminated, and a purer product results.—Greater control can be affected by carrying out the reaction at pH 9.0 and adding 2 *N* NaOH intermittently to maintain the pH at this value. F. e. s. A. L. Levy and D. Chung, Am. Soc. 77, 2899 (1955).

Amines from chlorides – Partial replacement

Cl → NHR

s. *6*, 464

Substitution of piperazines

NH → NR

s. *6*, 465

Ketimine methiodides

←

s. *9*, 516; cf. C. R. Hauser and D. S. Hoffenberg, Am. Soc. 77, 4885 (1955)

Selective N-acylation

NH → NAc

s. *9*, 517

Halogenocarboxylic acid amides

COCl → CONHR

s. *7*, 491

Sodium hydrogen carbonate

$NaHCO_3$

Sec. from prim. amines and halides

NH_2 → NHR

1,3,5-Triazine derivatives

s. *9*, 518

from fluorides

s. *8*, 563; s. a. F. Micheel, K. Weichbrodt, and J. Plenikowski, A. *581*, 238 (1953)

Subst. hydrazines
s. *9*, 988

Acylamines from amines $NH_2 \rightarrow NHAc$
Selective hydrolysis s. *6*, 466

N-Carbethoxyamidines ←
s. *6*, 237

Pyrrolidines from γ-dihalides ○
N-Pyrrolidylalkanols s. *6*, 467

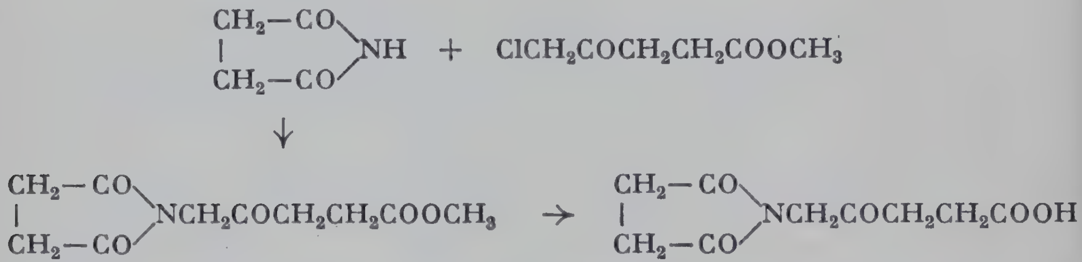
Potassium carbonate K_2CO_3

Tert. from sec. amines and halides $NH \rightarrow NR$

s. *2*, 439; with ethyl chloroacetate s. C. A. Grob and E. Renk, Helv. *37*, 1689 (1954)

Imidocarboxylic acids from halogenocarboxylic acid esters via imidocarboxylic acid esters ←

367.



Methyl δ-chlorolevulinate added to a gently warmed suspension of succinimide in dimethylformamide, then anhydrous K-carbonate added in small portions (to minimize the possibility of ring opening by excess of carbonate), shaken after each addition, the flask stoppered, allowed to stand overnight, and the reaction completed by warming to 60° for 1 hr. → methyl δ-succinimidolevulinate (Y: 88%) dissolved in 7 *N* HCl, allowed to stand 7 days at room temp., then warmed to 40°, and the product isolated → δ-succinimidolevulinic acid (Y: 92%). A. Neuberger and J. J. Scott, Soc. *1954*, 1820.

Peptide synthesis with N-phthalylaminoacid chlorides $COCl \rightarrow CONHR$
s. *8*, 511

Urethans from amines $NH_2 \rightarrow NHCOOR$
s. *9*, 519

Potassium hydrogen carbonate $KHCO_3$

Cyanohydrazides CONHNHCN
s. *6*, 468

Sodium acetate CH_3COONa

Sec. amines via α-bromocarboxylic acids ←
s. *8*, 512

α,β-Ethylenehydrazones from α-bromoketones ←
s. *6*, 891

α-Halogenocarboxylic acid amides CHalCONHR
s. *6*, 469

Quinoxalines ○
s. *7*, 492

Sodium azide NaN_3

Azides from halides Hal → N_3
s. 7, 493; s. a. J. H. Boyer and J. Hamer, Am. Soc. 77, 951 (1955)

α-Azidoketones
s. *9*, 485

Isocyanates from carboxylic acid chlorides via carboxylic acid azides COCl → N:C:O
Activation of sodium azide s. *6*, 470

Sodium salt Na^+

N-Alkylation NH → NR

of 2,4-oxazolidinediones
s. *9*, 24

of sulfimides
s. *9*, 520

(Diacylamino)carboxylic acid esters from acylaminocarboxylic acid esters via (carbalkoxyalkylimino)chlorides ←
s. *9*, 521

Isothiocyanates from halides Hal → NCS
s. *9*, 522

Glycocyamidines from cyanamides and carboxylic acid amides ○
s. *8*, 513

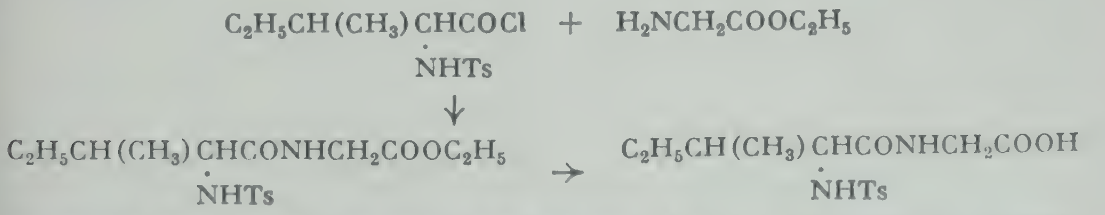
Potassium salt K^+

Bromoalkylphthalimides $Br \rightarrow N{<}^{OC|}_{OC|}$
s. *5*, 338; s. a. R. C. Elderfield et al., Am. Soc. 77, 4816 (1955)

Triethylamine $(C_2H_5)_3N$

Subst. carboxylic acid amides from carboxylic acid chlorides COCl → CONHR
s. *8*, 511

8.



$$C_2H_5CH(CH_3)\underset{NHTs}{CH}COCl + H_2NCH_2COOC_2H_5 \downarrow C_2H_5CH(CH_3)\underset{NHTs}{CH}CONHCH_2COOC_2H_5 \rightarrow C_2H_5CH(CH_3)\underset{NHTs}{CH}CONHCH_2COOH$$

Selective hydrolysis of carboxylic acid esters. A soln. of tosyl-L-isoleucyl chloride in anhydrous ether added slowly to a suspension of ethyl glycinate hydrochloride and triethylamine in ether, and allowed to stand 12 hrs. at room temp. → ethyl tosyl-L-isoleucylglycinate (Y: 89%) dissolved in ethanol, 1 *N* NaOH added, warmed 1 min. on a water bath at 70°, then allowed to stand 2 hrs. at room temp. → tosyl-L-isoleucylglycine (Y: 71%). F. e. s. P. G. Katsoyannis and V. du Vigneaud, Am. Soc. *76*, 3113 (1954).

Ethylenimino compounds ○
s. *8*, 514

Diethylaniline $C_6H_5N(C_2H_5)_2$

Urethans from amines NH → NCOOR
s. *6*, 586

N-Methylmorpholine ←

α-Halogenocarboxylic acid amides CHalCONHR
s. *6*, 308

Pyridine C_5H_5N

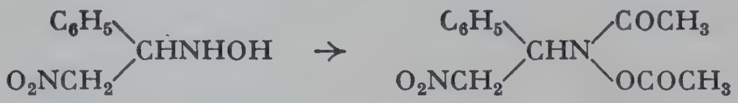
Tritylamines NH → NR
s. *9*, 523

Tert. from sec. amines via carboxylic acid amides
s. *9*, 524; 1,4-benzodioxan-2-carboxamides s. J. Koo, S. Avakian, and G. J. Martin, Am. Soc. *77*, 5373 (1955)

Sec. and tert. amides ←
s. *9*, 525

Mixed hydroxamic acid anhydrides from hydroxylamines ←

369.



$$(C_6H_5)(O_2NCH_2)CHNHOH \rightarrow (C_6H_5)(O_2NCH_2)CHN(COCH_3)(OCOCH_3)$$

Acetyl chloride in anhydrous dioxane added with cooling and shaking to a soln. of N-(1-phenyl-2-nitroethyl)hydroxylamine (prepn. s. 276) in dioxane-pyridine, and allowed to stand 15 min. at room temp. → acetic N-(1-phenyl-2-nitroethyl)acetohydroxamic anhydride. Y: 89%. F. e. and method s. C. D. Hurd and J. Patterson, Am. Soc. *75*, 285 (1953).

Halogenourethans from amines NH → NCOOR
s. *9*, 45

Sulfonylcyanamides from sulfonic acid chlorides $SO_2Cl \rightarrow SO_2NRCN$
s. *6*, 471

Copper *Cu*

N-Acylsulfonic acid amides SO_2NHAc
s. *6*, 472

Oxindoles
s. *9*, 527

Cupric oxide Cu_2O
Replacement of bromine by amino groups ←
Sec. from prim. amines and halides
s. *9*, 526

Silver hydroxide $AgOH$
N-Alkylbarbituric acids NH → NR
s. *6*, 473

Cupric acetate $(CH_3COO)_2Cu$
Oxindoles ○
s. *9*, 527

Silver azide AgN_3
Aceto-1-azido- from aceto-1-halogenosugars Hal → N_3
s. *5*, 340; 1-azido-2-glycosamines s. A. *581*, 161 (1953)

Silver nitrite $AgNO_2$
Aliphatic nitro compounds from halides Hal → NO_2
Victor Meyer reaction
Improved procedure s. *9*, 528

from iodides I → NO_2
s. *6*, 476

Calcium oxide CaO
Carboxylic acid amides from carboxylic acid chlorides COCl → CONHR
s. *7*, 495

Calcium carbonate $CaCO_3$
Sec. from prim. amines and halides NH_2 → NHR
s. *6*, 477

Halogenocarboxylic acid amides COCl → CONHR
s. *7*, 496

Magnesium oxide MgO
Subst. carboxylic acid amides from carboxylic acid chlorides COCl → CON<
s. *9*, 402

from carboxylic acids via carboxylic acid chlorides
Peptides
s. *5*, 341; s. a. E. A. Popenoe and V. du Vigneaud, Am. Soc. *76*, 6202 (1954)

Carbobenzoxylation of amines NH_2 → NHCOOR
s. *9*, 529

Magnesium oxide/pyridine MgO/C_5H_5N
α-Carbobenzoxyaminocarboxylic acid hydrazides from α-aminocarboxylic acid esters via α-carbobenzoxyaminocarboxylic acid esters ←
s. *8*, 515

Alkylmagnesium halide *RMgHal*

N-Acylation

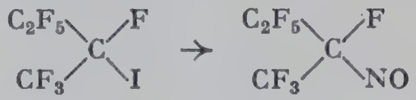
Acyliminonitriles from iminonitriles :NH → :NAc

s. 7, 494

Mercury/irradiation ←

Aliphatic nitroso compounds from iodides I → NO

370.



Perfluoronitroso compounds. A mixture of 2-perfluorobutyl iodide, Hg, and nitric oxide (NO) vigorously shaken 3-7 days in a sealed silica tube with irradiation → 2-nitrosoperfluorobutane. Y: 86%; conversion 23%. F. e. s. R. N. Haszeldine, Soc. *1953*, 2075.

Mercuric chloride *$HgCl_2$*

Glycosylimidazole ring via chloromercuriimidazole ring ←

Nucleosides s. 7, 497

Ethyl alcohol *C_2H_5OH*

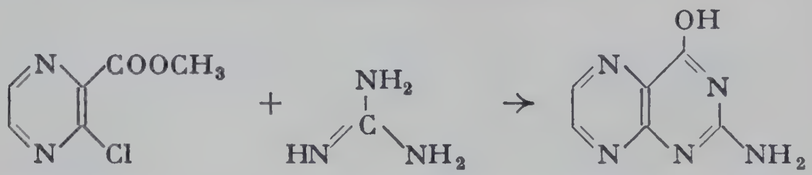
Diglycosamines from acetohalogenosugars ←

s. *9*, 530

Carbonate ←

2-Amino-4-hydroxypyrimido[4,5-b]pyrazines ○

371.



A mixture of methyl 2-chloropyrazine-3-carboxylate and guanidine carbonate heated 30 min. at a bath temp. of 170° with occasional stirring → 2-amino-4-hydroxypteridine. Y: 89%. F. e. s. G. P. G. Dick and H. C. S. Wood, Soc. *1955*, 1379.

Hexamethylenetetramine *$C_6H_{12}N_4$*

Prim. amines from halides Hal → NH_2

s. 2, 447; *6*, 478; s. a. A. Clavier, Bl. *1954*, 646

Aminomethylolsulfites from halides Hal → $NHCH_2OSO_2H$

s. 7, 499

Dimethylformamide *$HCON(CH_3)_2$*

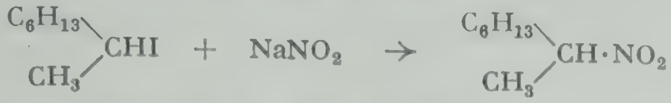
Phthalimides from halides – Gabriel synthesis Hal → $N\langle\begin{matrix}OC|\\OC|\end{matrix}$

s. *6*, 479; s. a. D. S. Popplewell and R. G. Wilkins, Soc. *1955*, 2521; from chlorides in the presence of KJ s. M. G. Ettlinger and J. E. Hodgkins, Am. Soc. *77*, 1831 (1955)

Urea *$OC(NH_2)_2$*

Aliphatic nitro compounds from halides Hal → NO_2

372.



$$\begin{matrix}C_6H_{13}\diagdown \\ CHI \\ CH_3\diagup\end{matrix} + NaNO_2 \rightarrow \begin{matrix}C_6H_{13}\diagdown \\ CH\cdot NO_2 \\ CH_3\diagup\end{matrix}$$

2-Iodoöctane added rapidly to dry $NaNO_2$ and urea in dry dimethylformamide, and stirred 4 hrs. at room temp. → 2-nitroöctane (Y: 60%) and 2-octyl nitrite (Y: 28%). F. e. s. N. Kornblum et al., Chem. & Ind. *1955*, 443.

Phenol/hydrochloric acid s. Hydrochloric acid/phenol *C_6H_5OH/HCl*

Lead salts *Pb^{++}*

Acylisothiocyanates from carboxylic acid chlorides COCl → CON:C:S
s. *6*, 480

Trichlorophosphazosulfonyl compounds ←

Nitriles from carboxylic acid halides COHal → CN
s. *8*, 517

Sulfuric acid *H_2SO_4*

N-Acylation NH → NAc
s. *10*, 390

Hydrochlorides ←

Hydroxylamines from halides Hal → NHOH
s. *9*, 531

Isocyanates from amines NH_2 → N:C:O
in toluene s. *1*, 385; in o-dichlorobenzene s. M. W. Miller, R. W. Amidon, and P. O. Tawney, Am. Soc. *77*, 2845 (1955)

Hydantoins from phosgene ○
s. *9*, 532

2,5-Oxazolidiones from α-aminocarboxylic acids
s. *8*, 518

Benz-3,1-oxazines
s. *7*, 498

Hydrochloric acid *HCl*

Pyrimidines, exchange of substituents ←
s. *8*, 519

N-Acylation NH → NAc
s. *10*, 390

Isonitrosoacetanilides NHCOCH:NOH
s. *8*, 520

Hydrochloric acid/phenol *HCl/C_6H_5OH*

Sec. from prim. amines and halides $NH_2 \rightarrow NHR$
s. *9*, 533

Via intermediates *v.i.*

Replacement of halogen by amino groups $Hal \rightarrow NH_2$
via aminomethylolsulfites
s. *7*, 499

Sulfur ↑ NC⇅S

Without additional reagents *w.a.r.*

N-Alkylation $NH_2 \rightarrow NR_2$
s. *8*, 521

Replacement of sulfur by amino groups ←
s. *9*, 542

Exchange of substituents of pyrimido[4,5-b]pyrazines ←
Replacement of sulfhydryl by amino groups
Sec. from prim. amines
s. *9*, 534

Amines from thioethers $SR \rightarrow NH_2$
s. *9*, 535

Carboxymethyl thioethers as intermediates
s. *6*, 482

Oxo compounds from thioenolethers via imines ←
s. *6*, 483

Sec. amines from sulfones $SO_2R \rightarrow NHR'$
s. *6*, 484; *7*, 500

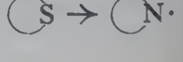
Replacement of sulfur by hydrazono groups $:S \rightarrow :N \cdot NH_2$
s. *8*, 522

Carboxylic acid thioamides $CSSR \rightarrow CSNHR$
from dithiocarboxylic acid esters
s. *7*, 501

Ureas and semicarbazides ←
from thiocarbonyl chlorides via S-thiocarbamic acid esters
s. *9*, 536

Thionocarbamic acid esters from thionothiodiformic acid esters ←
s. *9*, 537

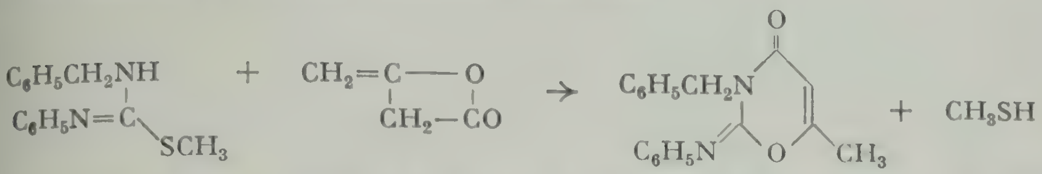
Replacement of cyclic sulfur by cyclic nitrogen
s. *8*, 523



New synthesis of purines from pyrimidines ○
s. *9*, 538; s. a. H. Bredereck and A. Edenhofer, B. *88*, 1306 (1955)

1,3-Oxazines from thioureas and diketene

73.



Diketene added during 0.5 hr. to a soln. of N-benzyl-S-methyl-N′-phenylthiourea in boiling ethylene dichloride, and refluxing continued for 2 hrs. → 3-benzyl-2,3-dihydro-6-methyl-4-oxo-2-phenylimino-1,3-oxazine. Y: 77%. F. e. s. R. N. Lacey, Soc. *1954*, 845.

Sodium *Na*

Substitution of carboxylic acid amides NHAc → NRAc
s. *6*, 502

Alkali hydroxide ←

N-Alkylation depending of pH NH → NR
purines with NaOH s. *6*, 485; pyrazolines with KOH s. J. Druey and P. Schmidt, Helv. *37*, 1828 (1954)

Sodium hydroxide *NaOH*

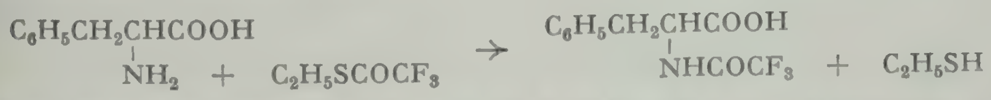
N-Alkylation
s. *6*, 410

Tert. from prim. and sec. amines and sulfonic acid esters $OSO_2R \rightarrow N\langle$
s. *7*, 435

Sec. amines from tosylamines NHTs → NHR
Selective N-alkylation
Lactam ring opening and closure
Blocking of amino groups by azomethine formation
s. *8*, 450

N-Trifluoroacetyl derivatives with ethyl thioltrifluoroacetate $NH \rightarrow N\cdot COCF_3$
Protection of amino groups

4.



$$\underset{NH_2}{C_6H_5CH_2CHCOOH} + C_2H_5SCOCF_3 \rightarrow \underset{NHCOCF_3}{C_6H_5CH_2CHCOOH} + C_2H_5SH$$

Ethyl thioltrifluoroacetate added to a soln. of L-phenylalanine in *N* NaOH, and the mixture shaken 24 hrs. whereby the resulting ethyl mercaptan is allowed to escape → N-trifluoroacetyl-L-phenylalanine. Y: 76.2%.—The use of ethyl thioltrifluoroacetate instead of trifluoroacetic anhydride is advantageous, because the reaction can be performed under mild conditions (pH 8-9) without racemization in the presence of water, and the volatility of ethyl mercaptan obviates any tedious purification scheme. The method may find application in the controlled formation of peptide bonds in aq. media. F. e., also peptides, s. E. E. Schallenberg and M. Calvin, Am. Soc. *77*, 2779 (1955).

Modified Gränacher synthesis CH(NH_2)COOH
α-Aminocarboxylic acids from rhodanines
via α-oximinocarboxylic acids
s. *8*, 524

α-Ketocarboxylic acid hydrazones from rhodanines ←
s. *8*, 525

Acylaminoguanidines from
carboxylic acid hydrazides and isothioureas ←
s. *6*, 409

Potassium hydroxide *KOH*

N-Methylation N·CH_3
4-Quinolones s. *8*, 526; 2-pyridones s. Y. Ahmad and D. H. Hey, Soc. *1954*, 4516

Thionocarbamic acid esters from ←
amines and dithiocarbonic acid O,S-diesters
s. *8*, 527

Oxazolidines from α-aminoalcohols ○
s. *7*, 502

2-Mercapto-benzimidazoles and -benzoxazoles
s. *6*, 486

Sodium/alcohol *NaOR*

Peptides via mixed alkoxyformic acid anhydrides COOH → CONHR
and thiolic acid esters
s. *8*, 528

Sodium methoxide

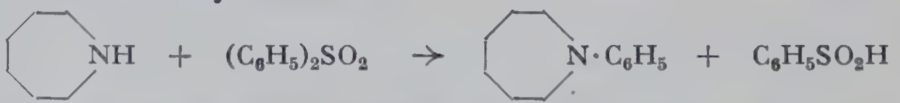
1,2,4-Triazoles from hydrazines ○
via thioformylhydrazines and 1,4-dihydro-1,2,4,5-tetrazines
s. *7*, 503

Sodium amide *$NaNH_2$*

N-Alkylation of indoles NH → NR
s. *9*, 539

Ar. amines from aryl sulfones NH → NAr

375.



Hexamethylenimine treated with xylene and $NaNH_2$ freshly powdered under xylene, refluxed 45 min., diphenyl sulfone added portionwise during 2 hrs., and refluxing continued for 16 hrs. → N-phenylhexamethylenimine. Y: 95%. H.-J. Nitzschke and H. Budka, B. *88*, 264 (1955); method s. W. Bradley, Soc. *1938*, 458.

Sodium hydrogen carbonate *$NaHCO_3$*

Selective N-methylation of ar. amines NH → NR
s. *9*, 540

Sodium acetate *CH_3COONa*

Oximes from acylthioenols CH:CHSAc → CH_2CH:NOH
s. *7*, 610

Coupling diazonium salts with sulfonium salts ←
1,2,3,4-Tetrazines s. *6*, 487

Alkali salts ←

ψ-2,4-Dihydro-1,3,4-thiadiazoles ○
Mesoionic rings s. *7*, 504

Sodium salt *Na^+*

Thiourethans from amines NH_2 → NHCSOR
s. *7*, 647

Thioformylhydrazines from hydrazines $NHNH_2$ → NHNHCHS
s. *7*, 503

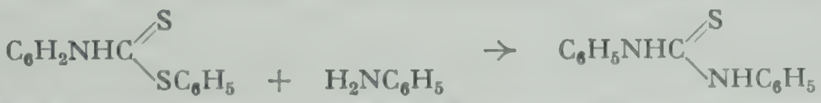
Triethylamine *$(C_2H_5)_3N$*

Subst. carboxylic acid thioamides from dithiocarboxylic acid esters CSSR → CSNHR′
s. *8*, 529; s. a. H. Hauptmann and H. Berl, Am. Soc. *77*, 704 (1955)

Disubst. ureas from S-thiocarbamic acid esters NHCOSR→NHCONHR′
s. *9*, 536

Thioureas from dithiocarbamic acid esters NHCSSR → NHCSNHR′

6.



$$C_6H_2NHC(=S)SC_6H_5 + H_2NC_6H_5 \rightarrow C_6H_5NHC(=S)NHC_6H_5$$

Aniline and triethylamine added to N.S-diphenyldithiocarbamate in dry dioxane, and allowed to stand for 1 hr. → N,N′-diphenylthiourea. Y: 82%. D. G. Crosby and C. Niemann, Am. Soc. *76*, 4458 (1954).

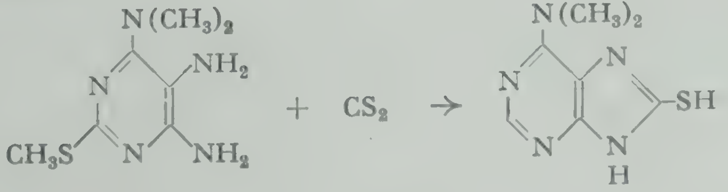
Peptides from 2-thiazolidinethiones C
s. *6*, 488

Pyridine *C_5H_5N*

Carboxylic acid anilides from carboxylic acids and sulfamides ←
Formamidines from sulfamides
s. *9*, 541; dicarboxylic acid dianilides s. Ж. *23*, 1920 (1953); C. A. *49*, 899h

Mercaptopurines ○

7.



A soln. of 2-methylmercapto-4,5-diamino-6-dimethylaminopyrimidine i pyridine and CS_2 refluxed 30 min. on a steam bath → 2-methylme capto-6-dimethylamino-8-mercaptopurine. Y: 91%. B. R. Baker, J. F Joseph, and R. E. Schaub, J. Org. Chem. *19*, 631 (1954); f. e. s. J. Org Chem. *19*, 638, 1793.

Mercuric oxide *Hg*

Replacement of sulfur by amino groups ←
s. *9*, 542

Pyrimidine ring from thioureas via guanidines ○
Purines from imidazoles
s. *7*, 505

Mercuric acetate *$(CH_3COO)_2Hg$*

Monosubst. thioureas NH_2 → $NHCSNH$
from amines via isothiocyanates
s. *8*, 530

Phosphate buffer pH 7.5 ←

Subst. carboxylic acid amides and peptides COSH → CONHR
from thiolic acids
s. *10*, 477

Lead acetate *$(CH_3COO)_2Pb$*

2-Oxazolidinethiones ○
s. *8*, 531

Sulfur *S*

Sym. thioureas from amines $CS(N\langle)_2$
s. *6*, 489

Sodium hypochlorite *NaOCl*

Subst. carboxylic acid thioamides CSSH → CSNHR
from dithiocarboxylic acids
s. *6*, 490

Sodium chlorate *$NaClO_3$*

Sec. from prim. amines and sulfonic acids SO_3H → NHR
s. *6*, 491

Hydrochlorides ←

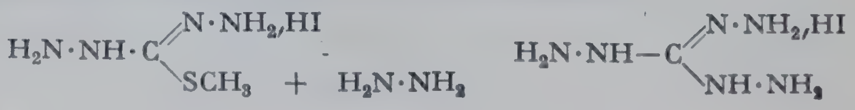
5-Aminoimidazoles from thioimidoesters ○
s. *7*, 506

Hydriodides ←

2-(Alkylamino)imidazolines SR → $N\langle$
s. *7*, 507

Hydrazinolysis SR → $NHNH_2$
Replacement of alkylthio by hydrazino groups

378.



$$H_2N\cdot NH\cdot C{\overset{\displaystyle N\cdot NH_2,HI}{\underset{\displaystyle SCH_3}{\lessgtr}}} + H_2N\cdot NH_2 \qquad H_2N\cdot NH-C{\overset{\displaystyle N\cdot NH_2,HI}{\underset{\displaystyle NH\cdot NH_2}{\lessgtr}}}$$

A refluxing soln. of S-methylisothiocarbohydrazide hydriodide in ethanol treated with 95%-hydrazine, heated 5 min. to assure complete reaction → triaminoguanidine hydriodide. Y: 82%.—The ease of hydrazinolysis increases in the order: $\rangle C{:}O < \rangle C{:}S < \rangle C{:}NH$ or $\rangle C\cdot NH_2 < \rangle C\cdot SR$. F. e. s. E. S. Scott and L. F. Audrieth, J. Org. Chem. *19*, 1231 (1954).

Aminoguanidines from isothioureas
s. *8*, 532

Via intermediates *v.i.*

Thionocarbamic acid esters H_2NCSOR
s. *8*, 533

Remaining Elements ↑ NC⇅Rem

Without additional reagents *w.a.r.*

Synthesis of peptides with phosphite amides COOH → CONHR
s. *9*, 543

Triethylamine *$(C_2H_5)_3N$*

Stepwise degradation of peptides via 2-thiohydantoins ○
Modified Schlack-Kumpf degradation
s. *9*, 544

Carbon ↑ NC⇅C

Without additional reagents *w.a.r.*

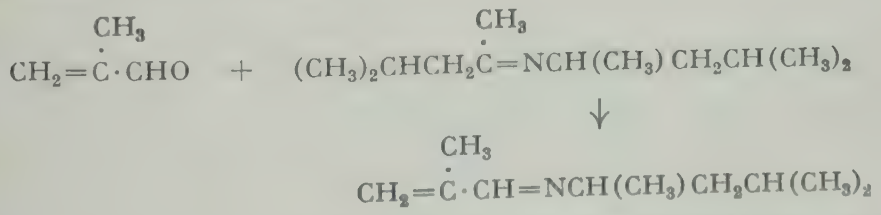
Replacement of carboxyl by nitro groups $COOH \rightarrow NO_2$
s. *8*, 534

Exchange of substituents in ureas ←
s. *6*, 492

Imidazole ring from imidazolone ring ←
Purines s. *6*, 493

Azomethines by interchange CO → C:NR

9.



$$CH_2{=}\overset{CH_3}{\dot{C}}\cdot CHO \quad + \quad (CH_3)_2CHCH_2\overset{CH_3}{\dot{C}}{=}NCH(CH_3)\,CH_2CH(CH_3)_2 \;\downarrow\; CH_2{=}\overset{CH_3}{\dot{C}}\cdot CH{=}NCH(CH_3)\,CH_2CH(CH_3)_2$$

A mixture of methacrolein and N-(1,3-dimethylbutylidene)-1,3-dimethylbutylamine allowed to stand at room temp. overnight, then warmed 4 hrs. at 50° → N-methallylidene-1,3-dimethylbutylamine. Y: 89%; conversion 83%. F. e. s. C. W. Smith, D. G. Norton, and S. A. Ballard, Am. Soc. *75*, 3316 (1953).

Thiosemicarbazones by interchange CO → C:NNHCSN
s. *9*, 432

Formylation of amines NH → NC
s. *9*, 545

Transamidation with dimethylformamide R_2NC

380. $C_6H_5COCl + HCON(CH_3)_2 \rightarrow C_6H_5CON(CH_3)_2$

A mixture of benzoyl chloride and dimethylformamide heated 4 hrs. 150° → N,N-dimethylbenzamide. Y: 97%. F. e. with carboxylic ac anhydrides in the presence of 1 drop of H_2SO_4, s. G. M. Coppinger, Ar Soc. *76*, 1372 (1954).

Acylamines from isocyanates N:C:O → NH
s. *7*, 508

Carboxylic acid carbamylamides

from 2 α-ketocarboxylic acid molecules
s. *7*, 509

from 2 α-acylamino-α,β-ethylenecarboxylic acid molecules
s. *7*, 509a

Sym. ureas CO (NHR
s. *8*, 535

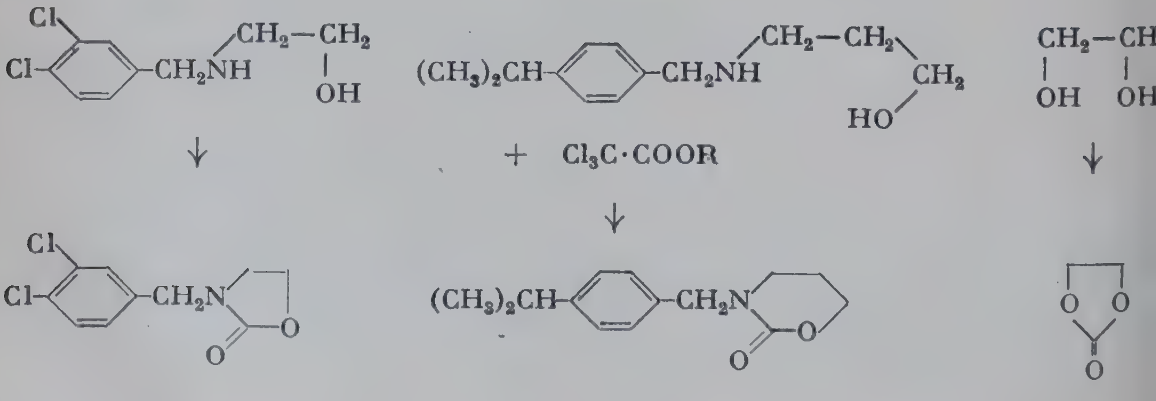
Dithiocarbamic from carbamic acid salts $NHCOO^- \rightarrow NHCSS$
s. *7*, 510

N-Subst. phthalimides from ureas
s. *6*, 494

Imidazolines from ketoxime sulfonates
s. *6*, 495

Synthesis of heterocyclics with trichloroacetic acid esters
3-Subst. 2-oxazolidones,
3-subst. tetrahydro-1,3,2H-oxazin-2-ones,
and cyclic carbonates

381.



A mixture of ethyl (or methyl) trichloroacetate,

and N-(3,4-dichlorobenzyl)-ethanolamine heated 4 hrs. on a steam bath → N-(3,4-dichlorobenzyl)-2-oxazolidone. Y: 84%.

and N-(4-isopropylbenzyl)-3-hydroxypropylamine heated 2-5 hrs. on a steam bath → N-(4-isopropylbenzyl)-2-pentoxazolidone. Y: 69%.

ethylene glycol, and 6 drops of pyridine heated 45 min. on a steam bath → ethylene carbonate. Y: 69%.

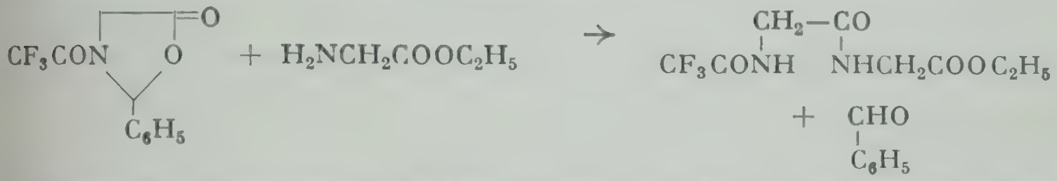
F. e. s. G. Y. Lesher and A. R. Surrey, Am. Soc. 77, 636 (1955).

1,3,5-Triazines from biguanides
s. *9*, 546

v. Braun degradation C
of quaternary ammonium salts by transalkylation
s. *9*, 547

Synthesis of peptides from 5-oxazolidones

82.



2-Phenyl-3-trifluoroacetyl-5-oxazolidone refluxed 1 hr. with glycine ethyl ester in tetrahydrofuran → N-trifluoroacetylglycylglycine ethyl ester. Y: 90%. F. Weygand and M. Reiher, B. 88, 26 (1955).

Amino-dithiocarbamic acids from imidazolines ←
s. *6*, 616

Sodium hydroxide *NaOH*

Indophenols ←
s. *6*, 496

Azo compounds by coupling $CH_2OH \rightarrow N{:}NR$
with elimination of formaldehyde
s. *6*, 497

Oxazole ring opening C
s. *10*, 266

Sodium/alcohol *NaOR*

α-Oximinocarboxylic acids $CH(COOR)_2 \rightarrow C(:NOH)COOH$
from malonic acid esters
s. *7*, 511

α-Oximinocarboxylic acid esters $CH(COOR)_2 \rightarrow C(:NOH)COOR$
from malonic acid esters
s. *6*, 823

Azo compounds from N-nitrosoacylamines N:N
s. *9*, 548

Sodium carbonate Na_2CO

Imidazole ring opening
s. *8*, 536

Sodium acetate CH_3COON

Hydrazones from diazonium salts ←
Japp-Klingemann reaction
s. *6*, 290; *8*, 537

Sodium nitrite $NaNO$

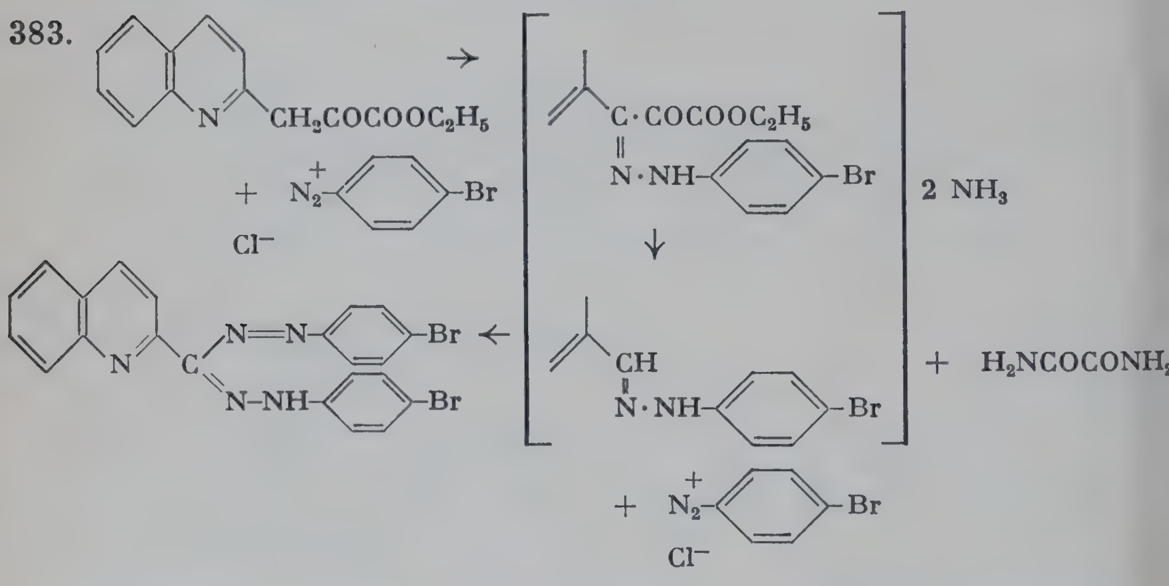
Replacement of hydroxymethyl by nitro groups $CH_2OH \rightarrow NO$
s. *6*, 498

Cleavage of di- and tri-arylmethane derivatives to azo compounds ←
s. *6*, 499; s. a. M. *84*, 610 (1953); s. a. V. V. Perekalin and L. P. Popova, ЖК. *24*, 1226, 1233 (1954); C. A. *49*, 12397b, e

Ammonia NH_3

Formazans from pyruvic acid esters ←

383.



$CH_2COCOOC_2H_5$
$+ \overset{+}{N_2}$ Br
Cl^-
$C\cdot COCOOC_2H_5$
N·NH– Br
2 NH_3
CH
N·NH– Br
+ $H_2NCOCONH_2$
N=N– Br
N–NH– Br
N
C
$+ \overset{+}{N_2}$ Br
Cl^-

p-Bromoaniline diazotized with $NaNO_2$ in aq. HCl, the diazonium salt soln. added at 0° with vigorous stirring to a mixture of ethyl 2-quinolyl-pyruvate, NH_3, water, and methanol, stirring continued for 2 hrs. → N,N′-di-(p-bromophenyl)-C-(quinolyl-2)-formazan. Crude Y: 79%. F. e. s. W. Ried and R. Hoffschmidt, A. *581*, 23 (1953).

Pyridine C_5H_5N

Subst. carboxylic acid amides from isocyanates N:C:O → NHCOR
Peptide synthesis
via α-isocyanatocarboxylic acid esters
s. *8*, 538

Cuprous phenylacetylenide *$C_6H_5C{:}C{\cdot}Cu$*

Formamidines from isonitriles NC → NHCH:NR

s. *8*, 539

Methylmagnesium iodide *CH_3MgI*

Replacement of N-acyl by N-alkyl NAc → NR

s. *9*, 549

Formic acid *HCOOH*

Oxazoles from α-formoxyketones ○

s. *10*, 330

Cyanogen bromide *CNBr*

Cyanamides from tert. amines NR → N·CN

s. *8*, 540

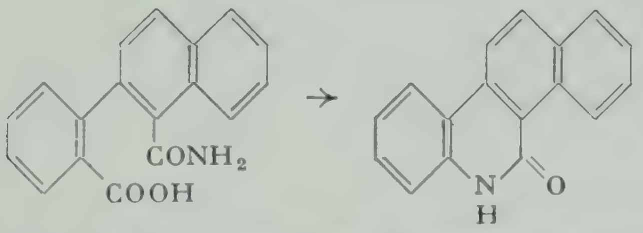
Hydrazoic acid *HN_3*

Schmidt reaction ←

α,ω-Diaminocarboxylic acids from α,ω-tricarboxylic acids COOH → NH_2

s. *8*, 541

84.



Phenanthridone ring closure. Powdered NaN_3 added gradually at 55-60° to a well stirred soln. of 2-o-carboxyphenyl-1-naphthoamide in concd. H_2SO_4, and kept an additional hr. at the same temp. → 7,8-benzophenanthridone. Y: 95%. G. M. Badger and J. H. Seidler, Soc. *1954*, 2329.

Phenanthridones from quinones

s. *10*, 279; s. a. S. Veibel and T. Bak, Acta Chem. Scand. *7*, 1127 (1953)

Hydroxylamine/polyphosphoric acid *$H_2NOH/H(PO_3H)_xOH$*

Amines from carboxylic acids COOH → NH_2

Lossen rearrangement

s. *8*, 542

Phosphorus oxychloride *$POCl_3$*

Exchange of substituents of amines NR → NR′

s. *9*, 625

Tosylates *TsOR*

1-Subst. quinazolones from 4-alkoxyquinazolines ←

s. *6*, 500

Sulfuric acid H_2SO_4

N-Sulfonylcarboxylic acid amides from N-sulfonylcyanamides ←

s. *6*, 501

Copper-chromium-barium oxide ←

Transalkylation of tert. amines NR → NR′

s. *9*, 550

Hydrochlorides ←

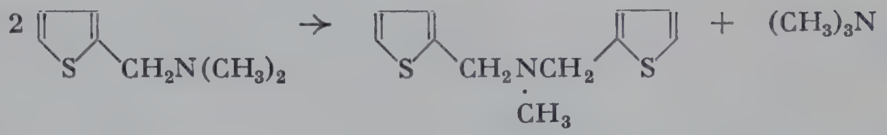
Subst. oxamidines ←

s. *6*, 451

Methiodides ←

Disproportionation of tert. amines ←

385.



A mixture of N,N-dimethyl-2-thenylamine and 1/10 the molar amount of its methiodide heated 18 hrs. at an oil bath temp. of 190° → N-methyl-di-2-thenylamine (Y: 56.5%) and trimethylamine.—Only amines of the benzyl type undergo this reaction. F. e. s. H. R. Snyder, R. E. Carnahan, and E. R. Lovejoy, Am. Soc. *76*, 1301 (1954).

Hydrochloric acid *HCl*

Lactam ring closure ○

s. *8*, 450

Via intermediates *v.i.*

Sec. amines from acylamines NHAc → NHR

s. *6*, 502

Shortened Curtius degradation COOH → NH_2

Amines from carboxylic acids

via acid chlorides, acid azides, and sym. ureas

s. *9*, 551

Elimination

Hydrogen ↑ NC⇑H

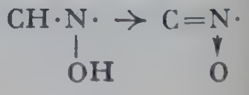
Mercuric oxide *HgO*

Dehydrogenation of dihydro-N-heterocyclics ←

s. *8*, 778

Nitrones from hydroxylamines

s. *10*, 61



$$\underset{\substack{|\\ OH}}{CH\cdot N\cdot} \rightarrow \underset{\substack{\downarrow\\ O}}{C{=}N\cdot}$$

Tetramethylammonium acetate $CH_3COON(CH_3)_4$

Indazoles from diazonium salts of N-nitrosoacylamines – Intramolecular coupling ○

s. *9*, 552; in pyridine cf. A. *586*, 84 (1954)

Hexamethylenetetramine $C_6H_{12}N_4$

Azomethines from sec. amines $CH_2NHR \rightarrow CH{:}NR$

s. *8*, 835

Nitrobenzene/sodium hydroxide $C_6H_5NO_2/NaOH$

Aldehydes from quaternary ammonium salts via hydroxylamines and nitrones $CH_2N^+R_3 \rightarrow CHO$

s. *9*, 553; cf. B. *88*, 418 (1955)

Red lead oxide Pb_3O_4

Quinone diimides from arylenediamides and reverse reaction ←

s. *7*, 512

Lead tetraacetate $(CH_3COO)_4Pb$

Quinone monoimides from sulfonylaminophenols ←

s. *8*, 543

Quinone diimides from arylenediamides and reverse reaction ←

s. *7*, 512; quinone diimides s. a. Am. Soc. *77*, 5375 (1955)

Benzimidazoles and benzoxazoles from azomethines ○

s. *6*, 503

Lead dioxide PbO_2

Quinone disulfonimides from arylenedisulfonamides ←

s. *7*, 513

Oxygen O_2

Glyoxylamidine anils from Sabaneyev bases ←

s. *10*, 641

Hydrogen peroxide H_2O_2

Quinoxalines from 1,2,3,4-tetrahydroquinoxalines ←

s. *6*, 514

Hydrogen peroxide/ferrous chloride $H_2O_2/FeCl_2$

s. Ferrous chloride/hydrogen peroxide

Chromium-copper-carbon $Cr\text{-}Cu\text{-}C$

Dehydrocyclization and dehydrogenation ←

s. *8*, 544

Chromic acid CrO_3

Pyridines from 1,4-dihydropyridines ←

s. *8*, 814

Iodic acid HIO_3

Aminochromes with simultaneous iodination ○

s. *8*, 545

Ferrous chloride/hydrogen peroxide *$FeCl_2/H_2O_2$*

Quinoxalines from dihydroquinoxalines ←

s. *8*, 409

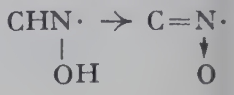
Ferric chloride *$FeCl_3$*

3-Mercapto-1,2,4-triazoles from thiosemicarbazones via isothiosemicarbazones ○

s. *9*, 554

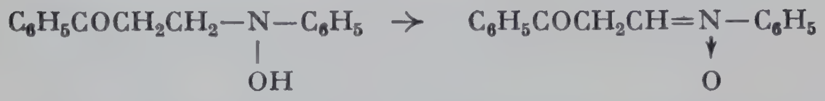
Potassium ferricyanide *$K_3[Fe(CN)_6]$*

Nitrones from hydroxylamines



$\underset{OH}{CHN\cdot} \rightarrow \underset{O}{C{=}N\cdot}$

386.



$C_6H_5COCH_2CH_2-\underset{OH}{N}-C_6H_5 \rightarrow C_6H_5COCH_2CH{=}\underset{O}{N}-C_6H_5$

A soln. of N-phenyl-N-(3-oxo-3-phenylpropyl)hydroxylamine in chloroform shaken 25 min. with a soln. of the calculated amount (2 moles) of K-ferricyanide and $NaHCO_3$ in water → ω-formylacetophenone phenylaldonitrone. Y: 82-91%. F. e. s. J. Thesing, A. Müller, and G. Michel, B. *88*, 1027 (1955).

Indoles from aminochromes ○

s. *7*, 514

Palladium-carbon *Pd-C*

Dehydrogenation of dihydro-N-heterocyclics ←

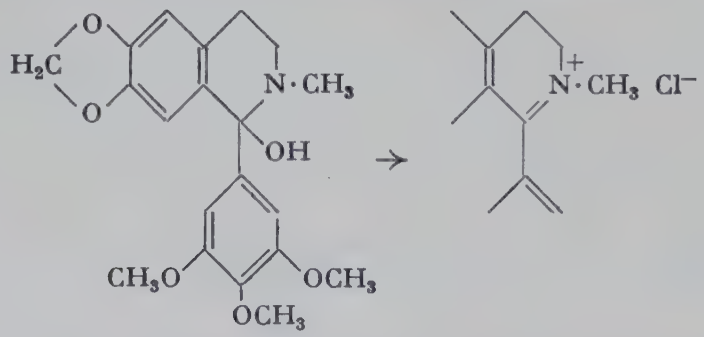
s. *8*, 546

Oxygen ↓ NC⇑O

Without additional reagents *w.a.r.*

Cyclic quaternary ammonium salts from pseudobases ←

387.



Concd. HCl added to the soln. of the carbinolamine in acetone, then kept overnight at -4° → 1-(3′,4′,5′-trimethoxyphenyl-2-methyl-6,7-methylene-dioxy-3,4-dihydroisoquinolinium chloride. Y: 93%. W. J. Gensler and C. M. Samour, Am. Soc. *74*, 2959 (1952).

Low molecular isocyanates from urethans NHCOOR → N:C:O

s. *6*, 504

Lactam ring closure
s. *9*, 949

Racemization via lactams
s. *9*, 555

m-Ring closure of N-heterocyclics
s. *6*, 505

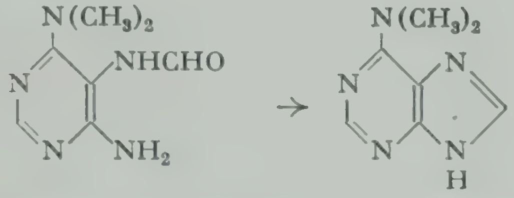
Indolizidones s. *8*, 547	**Pyrazole ring** s. *8*, 548

Indazoles from N-nitrosoacylamines
s. *9*, 552; s. a. A. *586*, 84 (1954)

Imidazoles
s. *7*, 469

Purines from pyrimidines

388.

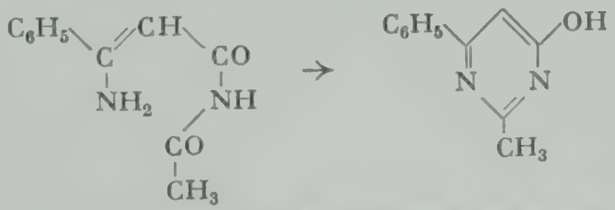


Crude 4-amino-5-formamido-6-dimethylaminopyrimidine heated 5 min. in a bath at 250-255° → 6-dimethylaminopurine. Y: 85%. B. R. Baker, J. P. Joseph, and R. E. Schaub, J. Org. Chem. *19*, 631 (1954); f. e. s. J. Org. Chem. *19*, 1793.

Benzoxazoles s. *9*, 558	**Pyridazinones** s. *7*, 515

Pyrimidine ring closure

89.



0.6 g. N-β-aminocinnamoylacetamide boiled 2 hrs. with water → 0.5 g. 6-hydroxy-2-methyl-4-phenylpyrimidine. F. e. s. G. Shaw and G. Sugowdz, Soc. *1954*, 665; *1955*, 1834.

2,5-Piperazinediones
s. *9*, 556

N-Condensed heterocyclics
s. *9*, 557

One-step purine synthesis
s. *7*, 516

2,3,6,7-Tetrahydrothiazolo[3,2-a]pyrimidines
s. *6*, 506

Sodium *Na*

2,4-Oxazolidiones from isocyanates via urethans
s. *7*, 517

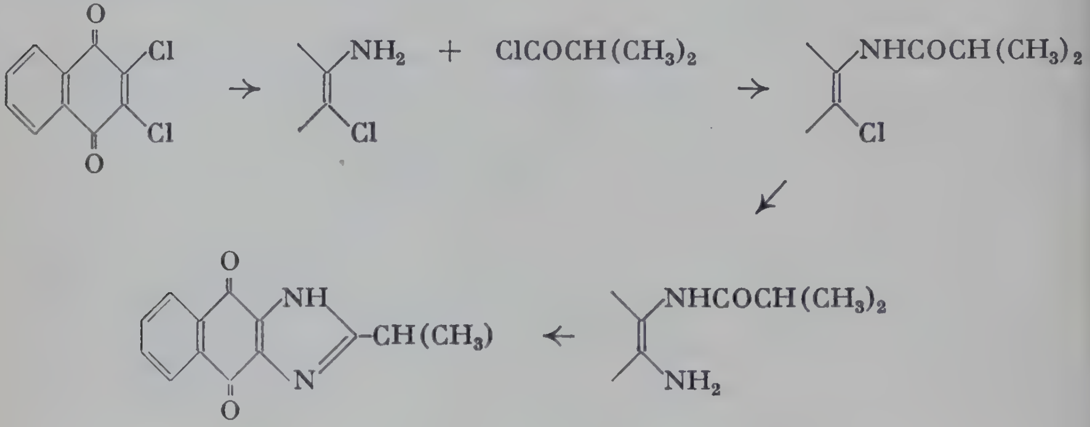
Sodium hydroxide *NaOH*

Cyclic imines from aminosulfuric acid esters
s. *6*, 507; by flash distillation s. *7*, 518

Dicarboxylic acid imides from cyanocarboxylic acid esters via dicarboxylic acid amide esters
s. *9*, 559

Imidazole ring
Replacement, also partial, of chlorine by prim. amino groups
N-Acylation

390.



1H-Naphthimidazole-4,9-diones. A slow NH_3-stream passed 90 min. into a refluxing mixture of 2,3-dichloro-1,4-naphthoquinone in ethanol and concd. aq. NH_3 → 2-amino-3-chloro-1,4-naphthoquinone (Y: 74%) refluxed with isobutyryl chloride in the presence of HCl and with addition of xylene to raise the reflux temp. → 2-isobutyrylamino-3-chloro-1,4-naphthoquinone (Y: 84%) dissolved in nitrobenzene, and treated 1 hr. with dry NH_3 at 145-150° → 2-isobutyrylamino-3-amino-1,4-naphtoquinone (Y: 86%), a hot soln. in alcohol treated with 2 *N* NaOH and heated 15-20 min. → 2-isopropyl-1H-naphthimidazole-4,9-dione (Y: 83%). F. e., also N-acylation with H_2SO_4 as catalyst, amination in dioxane, and ring closure in glacial acetic acid under reducing conditions (Pd-black, H_2), s. J. R. E. Hoover and A. R. Day, Am. Soc. *76*, 4148 (1954).

Purines from imidazoles

Pyrimidine ring via thioureas
s. *7*, 519

Thiazolo[5,4-d]pyrimidines
s. *6*, 508

1,3-Thiazines
s. *8*, 549

1,2,3-Triazines
s. *6*, 509

Potassium hydroxide KOH

1,3,5-Triazines from acylbiurets
s. *9*, 560

Sodium/alcohol $NaOR$

2-Pyrrolones via azomethines
s. *8*, 550

Pyrimido[4,5-b]pyrazines from pyrazines
s. *9*, 561

1,2,4-Triazoles from acylthiosemicarbazides
s. *6*, 510

Potassium/alcohol KOR

2-Pyrrolines
α-Aminomethylene compounds
from α-hydroxymethylene compounds
s. 6, 511

1,2-Dihydroimidazo[1,2-a]pyrroles
from aminomethylene compounds via α-aminopyrroles
s. *6*, 374

Sodium carbonate Na_2CO_3

1,2,3-Triazoles
s. *6*, 509

Sodium hydrogen carbonate $NaHCO_3$

Piperidone ring closure
s. *7*, 567

Potassium carbonate K_2CO_3

1,2,3,4-Tetrahydropyridine ring
s. *8*, 551

2-Thio-1,2-dihydropyrimidines
s. *8*, 552

Potassium hydrogen carbonate $KHCO_3$

Purines from imidazoles ¬ Formamides
s. *7*, 520

Sodium acetate CH_3COONa

Dicarboxylic acid imides
from dicarboxylic acid monoamides
s. *7*, 521

Lithium chloride/phosphorus pentoxide $LiCl/P_2O_5$
s. Phosphorus pentoxide/lithium chloride

Sodium chloride/phosphorus oxychloride $NaCl/POCl_3$
s. Phosphorus oxychloride/sodium chloride

Ammonia *NH_3*

1,3,5-Triazines from carbalkoxydicyanodiamides via carbalkoxyguanylureas
s. *9*, 562

Triethylamine/ethyl chloroformate *$(C_2H_5)_3N/ClCOOC_2H_5$*
s. Ethyl chloroformate/triethylamine

Pyridine *C_5H_5N*

N-Sulfonylcyanamides from ureas $NHCONH_2 \rightarrow N{<}\genfrac{}{}{0pt}{}{CN}{SO_2R}$
s. *6*, 333

2-Pyrrolidones ○
s. *10*, 636

Pyridine *$C_5H_5N/RCOCl$*
s. under Carboxylic acid chloride, Arylsulfonyl chloride, p. Toluenesulfonyl chloride

Lithium aluminum hydride/platinum-asbestos ←
s. Platinum-asbestos/lithium aluminum hydride

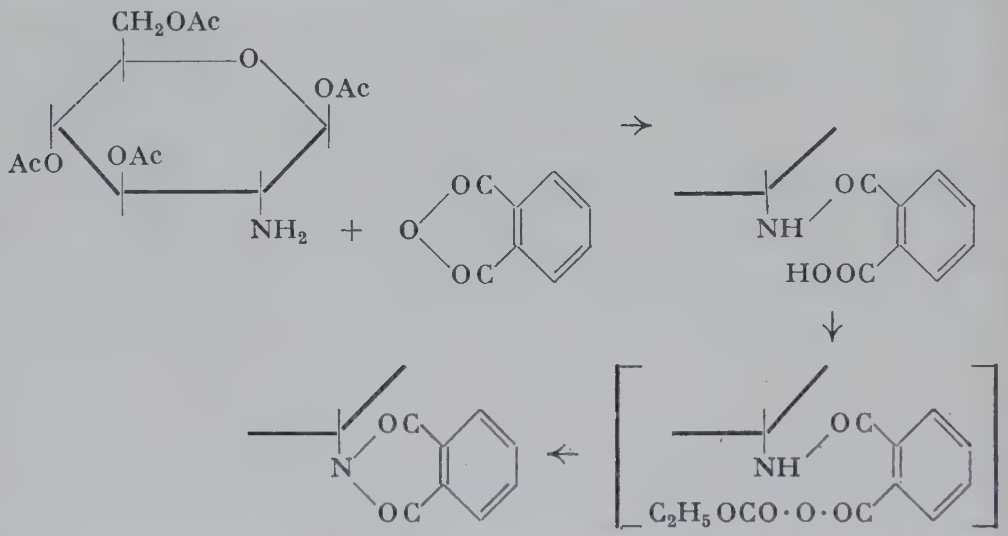
Alumina-silica *Al_2O_3-SiO_2*

Nitriles from carboxylic acid amides $CONH_2 \rightarrow CN$
s. *9*, 563

Ethyl chloroformate/triethylamine *$ClCOOC_2H_5/(C_2H_5)_3N$*

Phthalimides from prim. amines via phthalamic acids $NH_2 \rightarrow N{<}\genfrac{}{}{0pt}{}{OC}{OC}$
Mild two-step procedure
Mixed alkoxyformic acid anhydrides as intermediates

391.



A soln. of phthalic anhydride in chloroform added to a soln. of 1,3,4,6-tetraacetyl-β-D-glucosamine in the same solvent, and refluxed 30 min. → 2-(o-carboxybenzamido)-β-D-glucopyranose tetraacetate (Y: 85%) dissolved with triethylamine in chloroform, ethyl chloroformate added with ice-cooling, and allowed to stand 1.5 hrs. at room temp. → 2-

phthalimido-β-D-glucopyranose tetraacetate (Y: 74%). F. e. s. B. R. Baker et al., J. Org. Chem. *19*, 1786 (1954).

Acetic anhydride $(CH_3CO)_2O$

Nitriles from carboxylic acid amides $CONH_2 \rightarrow CN$
s. *6*, 513

Dioxindole derivatives ○
s. *9*, 564

Anhydro-N-heterocyclic thioglycolic acids
Mesoionic rings s. *7*, 522

Carboxylic acid chloride/pyridine $RCOCl/C_5H_5N$

Nitriles from carboxylic acid amides $CONH_2 \rightarrow CN$
s. *9*, 525

Tin Sn

Quinoxalines via 1,2,3,4-tetrahydroquinoxalines ○
Reductive ring closure
s. *6*, 514

Lead/ferrous oxalate s. Ferrous oxalate/lead Pb/FeC_2O_4

Phosphorus pentoxide/lithium chloride $P_2O_5/LiCl$

Nitriles from carboxylic acid amides $CONH_2 \rightarrow CN$
Labeled compounds s. *8*, 553

Phosphoric acid H_3PO_4

Indolizine ring closure ○
s. *8*, 554

Phosphorus trichloride PCl_3

Nitriles from carboxylic acid amides $CONH_2 \rightarrow CN$
s. *9*, 565

Phosphorus oxychloride $POCl_3$

Purines from pyrimidines ○
s. *8*, 555

Phosphorus oxychloride/sodium chloride $POCl_3/NaCl$

Nitriles from carboxylic acid amides $CONH_2 \rightarrow CN$
s. *5*, 359; in ethylene dichloride s. E. A. Schildknecht and E. V. Brown, Am. Soc. *77*, 954 (1955)

Phosphorus pentachloride PCl_5
s. *6*, 515

Lactam ring closure with simultaneous formation of carboxylic acid chlorides from carboxylic acids ○
s. *9*, 566

Ammonium sulfide $(NH_4)_2S$

5,7,12,14-Tetraazapentacene-6,13-quinones
via 5,12-dihydro-5,7,12,14-tetraazapentacenes
Reductive acylation of N-heterocyclics
s. *8*, 556

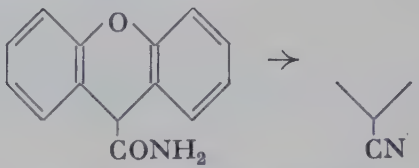
Hydrosulfite $S_2O_4^-$

Reductive ring closure of N-heterocyclics
s. *7*, 886

Arylsulfonyl chlorides/pyridine $ArSO_2Cl/C_5H_5$

Nitriles from carboxylic acid amides $CONH_2 \rightarrow C$

392.



under mild conditions. A soln. of 9-xanthene carboxamide in excess pyridine treated with excess of either benzene- or p-toluene-sulfonyl chloride with temp. control, after 5-10 min. when the exothermic reaction subsides cooled to 25° and poured into excess water → 9-xanthenylcyanide. Y: 82%.—The usual methods give poor yields. F. e. and procedure s. C. R. Stephens, E. J. Bianco, and F. J. Pilgrim, Am. Soc. 77, 1701 (1955).

p-Toluenesulfonyl chloride/pyridine

Disubst. cyanamides from ureas $R_2NCONH_2 \rightarrow R_2NCN$
s. *6*, 512; s. a. J. R. Robinson, Can. J. Chem. *32*, 901 (1954)

Ammonium sulfamate $H_2NSO_2ONH_4$

Nitriles from carboxylic acid amides $CONH_2 \rightarrow CN$
s. *7*, 524

Sulfamic acid HSO_3NH_2

s. *6*, 516

Hydroxylaminedisulfonate $HON(SO_3)_2^{--}$

Oximes from nitro compounds $CH(NO_2) \rightarrow C{:}NOH$
s. *6*, 517

Sulfuric acid H_2SO_4

Pyrido[1,2-a]pyrimid-2-ones ○
s. *7*, 525

Chlorosulfonic acid/potassium hydroxide $ClSO_3H/KOH$

Cyclic imines from aminoalcohols
s. *6*, 518

Copper chromite $CuCr_2O_4$

Decahydrodipyrrolo[a,d]pyrazines
Alcohols from carboxylic acid esters
s. *9*, 567

Hydrochlorides ←

Imidazoles via azo compounds and formamides
s. *6*, 519

2-Imino-1,3,2H-thiazines from α,β-ethylenisothiouronium salts
s. *8*, 557

Hydrochloric acid *HCl*

Imidazole ring
s. *8*, 558

Hydantoins from α-ureidocarboxylic acids
s. *9*, 404; in abs. alcohol with simultaneous esterification s. A. Dornow and K. Rombusch, B. *88*, 1334 (1955)

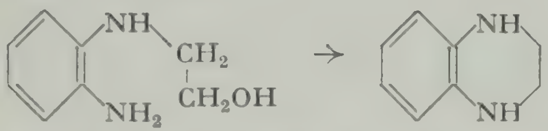
Hydantoins from N-carbalkoxypeptides via α-ureidocarboxylic acids
Differentiation between α- and γ-glutamyl peptides
Degradation of peptides via hydantoins
s. *9*, 568

2-Thiohydantoins from thioureas
s. *7*, 526

Neber-Bossel 3-hydroxycinnoline ring synthesis
s. *9*, 569

2,4-Quinazolinediones
s. *7*, 527

1,2,3,4-Tetrahydroquinoxalines

93. 

2 g. o-amino-N-2-hydroxyethylaniline and concd. HCl heated 15 hrs. at 150-160° in a sealed tube → 0.93 g. 1,2,3,4-tetrahydroquinoxaline. F. e. s. G. R. Ramage and G. Trappe, Soc. *1952*, 4406.

Pyrrolo(2′,3′:3,4)isocoumarins as intermediates
s. *9*, 740

1,3,4-Thiadiazines from α-(dithiocarbazyl)oxo compounds
s. *9*, 697

Hydrobromic acid *HBr*

β-Lactams
s. *6*, 520

Different reactivity of halides
s. *9*, 570

6,7,8,9-Tetrahydropyrido[1,2-a]benzimidazoles
s. *8*, 559

Pyrido[1,2-a]pyrimidin-2-ones
s. *9*, 571

Ferrous oxalate/lead *FeC_2O_4/Pb*

Phenazines from nitrodiphenylamines
s. *7*, 523

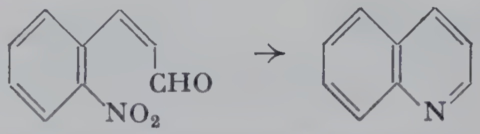
Ferrous sulfate/ammonia *FeSO$_4$/NH$_3$*

Indoles

s. *5*, 363; s. a. H. Singer and W. Shive, J. Org. Chem. *20*, 1458 (1955); Am. Soc. *77*, 5700 (1955); H. N. Rydon and J. C. Tweddle, Soc. *1955*, 3499; in alcohol-water s. H. R. Snyder and H. R. Beilfuss, Am. Soc. *75*, 4921 (1953).

Quinolines

394.



Aq. NH$_3$ (d. 0.88) added portionwise with vigorous shaking to a mixture of o-nitrocinnamaldehyde (prepn. s. 135), ferrous sulfate, HCl, and water, heated to 90° under reflux, heating continued for 1 hr., then steam-distilled → quinoline. Y: 82%. W. Davey and J. R. Gwilt, Soc. *1955*, 1384.

Potassium ferricyanide *K$_3$[Fe(CN)$_6$]*

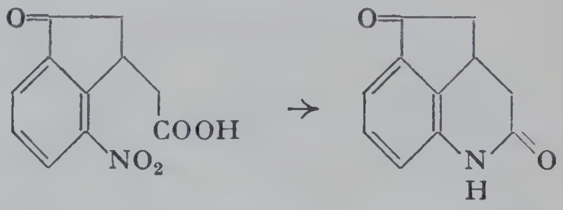
Hydroxyindoles

s. *9*, 572

Nickel *Ni*

Reductive ring closure to N-heterocyclics

395.



4-Nitroindan-1-one-3-acetic acid hydrogenated 16 hrs. with Raney-Ni in 95%-ethanol at 3 atm. and room temp. → tricyclic compound. Y: 91%. R. C. Fuson and T. M. Veazey, Am. Soc. *76*, 1169 (1954).

s a. *8*, 560; F. Šorm and J. Beránek, Coll. Czech. Chem. Communs. *19*, 298 (1954); V. V. Perekalin and A. S. Sopova, Ж. *24*, 513 (1954); C. A. *49*, 6180g

2-Pyrrolidones from nitronitriles

s. *6*, 521

Piperidines

s. *6*, 522; *8*, 561

of cyanoketones

to piperidines s. *6*, 522; to $\Delta^{9,10}$-octahydroisoquinolines s. A. *583*, 110 (1953)

Pyrrolo[2,1-b]quinazoline ring

s. *6*, 523

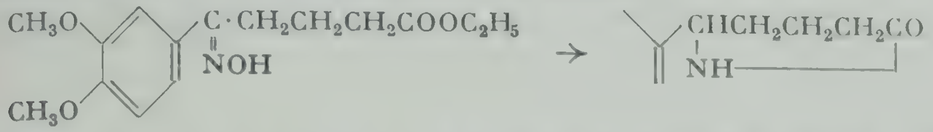
Palladium *Pd*

s. *9*, 573

Palladium-carbon *Pd-C*

Lactams from oximinocarboxylic acid esters

96.

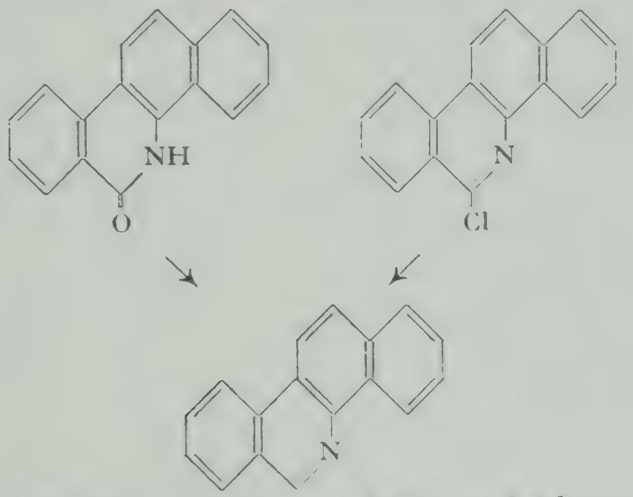


A soln. of ethyl δ-oximino-δ-(3,4-dimethoxyphenyl)valerate in acetic acid hydrogenated with 5%-Pd-on-carbon at room temp. and 40 lb. pressure until after 1 hr. the theoretical amount of H_2 has been absorbed → δ-amino-δ-(3,4-dimethoxyphenyl)valeric acid lactam. Y: 98%. J. Koo, Am. Soc. *75*, 723 (1953).

Platinum-asbestos/lithium aluminum hydride ←

Phenanthridines from ←
phenanthridones and 6-chlorophenanthridines

97.



3,4-Benzophenanthridone | 6-Chloro-3,4-benzophenanthridine

and $LiAlH_4$ in dry dioxane refluxed

10 hrs. | 8 hrs.

and the unstable dihydride dehydrogenated by heating 2 hrs. with 10%-platinized asbestos in p-cymene → 3,4-benzophenanthridine.

Y: 95%. | Y: almost 100%.

F. e. s. G. M. Badger and J. H. Seidler, Soc. *1954*, 2329.

Platium oxide *PtO_2*

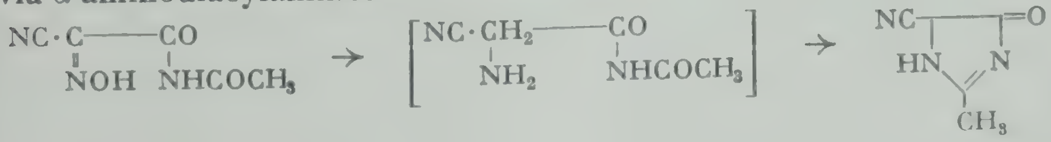
○

Reductive ring closure to N-heterocyclics

Indoles	**Indoloquinolines**
s. *6*, 524	s. *7*, 528

Imidazolines from α-oximino-diacylamines via α-aminodiacylamines

8.



A soln. of 1 g. N-acetyl-α-cyano-α-oximinoacetamide in ethanol hydrogenated 5 hrs. with PtO_2, filtered, and evaporated to dryness in vacuo → 0.7 g. 5-cyano-1,5-dihydro-2-methyl-4-oxoglyoxaline.—F. e., also with isolation of the intermediate, s. G. Shaw, Soc. *1955*, 1834.

Via intermediates *v.i.*

N-Heterocyclics from aminoethers via halogenamines
s. *7*, 529

Phenanthridines from phenanthridones via phenanthrithiones
s. *9*, 574

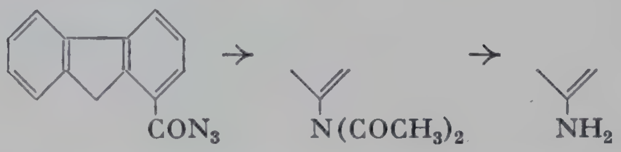
Pyrimidine ring from guanidines
Purines from imidazoles
s. *7*, 505

Nitrogen ⇑ NC⇑N

Without additional reagents *w.a.r.*

Amines from carboxylic acid azides via diacylamines $CON_3 \rightarrow NH_2$
Modified Curtius degradation

399.



A soln. of 51 g. 1-fluorenecarbonyl azide in acetic anhydride warmed gently until gas-evolution slows down, then refluxed 4 hrs. → 56 g. 1-diacetylaminofluorene, 10 g. refluxed 1 hr. with concd. HCl-ethanol → 6.8 g. 1-aminofluorene.—This modification seems to be useful in cases where the intermediate isocyanates or urethans are difficult to hydrolyze. E. K. and J. H. Weisburger, J. Org. Chem. *18*, 864 (1953).

Low molecular isocyanates from ureas NHCON< → N:C:O
s. *6*, 525

Arylisothiocyanates from arylthioureas $NHCSNH_2$ → N:C:S
s. *9*, 575

N-Heterocyclics from azides ○
s. *8*, 562

Carbazoles
s. *7*, 530

New stepwise degradation of peptides ←
by formation of 3,4-dihydro-2-quinoxalones
s. *8*, 563

Azacyclopropanes from 1,2,3-triazolines ←
s. *7*, 704

Irradiation ←

Isatogens from cyclic quaternary hydroxyammonium salts ○
s. *9*, 733

Sodium hydroxide *NaOH*

Isocyanates from ureas $NHCONH_2 \rightarrow N{:}C{:}O$
s. *10*, 256

Sodium carbonate *Na_2CO_3*

Isatogens from cyclic quaternary ammonium salts ○
s. *8*, 564

Quinoline ←

Ring closure of N-heterocyclics with elimination of nitrous acid
s. *8*, 565

Acetyl chloride *CH_3COCl*

Benzimidazoles
s. *6*, 526

Hydrochlorides ←

9,10-Dihydro-2,9,10-triazaanthracenes
s. *6*, 527

Ferric chloride *$FeCl_3$*

Isothiocyanates from thiosemicarbazides $NHCSNHNH_2 \rightarrow N{:}C{:}S$
s. *7*, 531

Phenazines – Amines from nitro compounds ○
s. *7*, 532

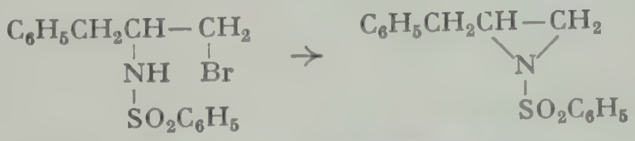
Halogen ↑ NC⇑Hal

Without additional reagents *w.a.r.*

Imidazolines from guanidines ○
s. *6*, 528

Sodium hydroxide *NaOH*

Cyclic imines from halogenamines



A mixture of 1-phenyl-2-benzenesulfonamido-3-bromopropane, NaOH, and water shaken 15 min. → 1-benzenesulfonyl-2-benzylethylenimine. Y: 81-95%. W. J. Gensler and J. C. Rockett, Am. Soc. *74*, 4451 (1952).

Benz[cd]indolines
s. *7*, 533

Isothiazolidine 1,1-dioxides
s. *7*, 534

Potassium hydroxide K

Imidazolidines and oxazolidines
s. *8*, 566

2-Oxazolidones from halogenourethans
s. *9*, 45

Potassium hydroxide/alcohol

N-Heterocyclics from halogenamines
s. *7*, 529

Isocarbostyrils
s. *9*, 576

Sodium/alcohol Na

Imines from N-halogenamines CHNHHal → C:
s. *10*, 257, 298

2-Piperidones
s. *7*, 535

Sodium amide Na

N-Allyllideneamines
s. *8*, 567

Sodium hydrogen carbonate NaH

4-Thiazolinecarboxylic acids from inner isothiouronium salts
s. *8*, 653

Pyridine C_5

Isocyanates from carbamyl chlorides NHCOCl → N:
s. *6*, 455

Sulfur ↑ NC

Sodium hydroxide Na

1-Subst. 2-aminobenzimidazoles from 2-sulfonylaminobenzimidazoles
s. *7*, 536

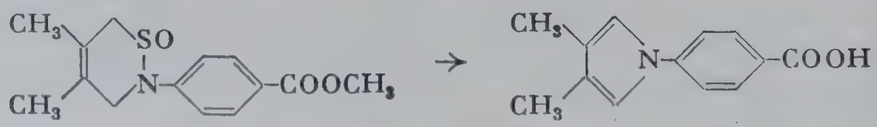
2-Thiazolidones from dithiolcarbonic acid esters
s. *9*, 577

Potassium hydroxide/alcohol K

Naphthostyrils from cyanosulfonic acids with simultaneous replacement of sulfonic acid groups by hydroxyl
s. *7*, 537

Pyrroles from 1,2-thiazine 1-oxides

401.



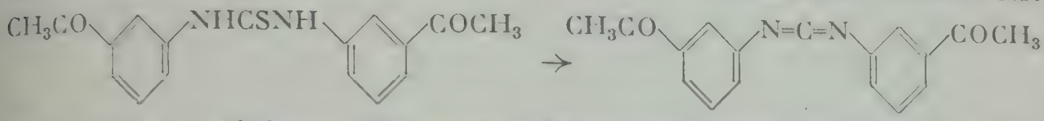
4,5-Dimethyl-2-(4′-carbomethoxyphenyl)-3,6-dihydro-1-oxo-1,2-thiaz
refluxed 1.5 hrs. with a soln. of KOH in ethanol → 1-(4′-carbo

phenyl)-3,4-dimethylpyrrole. Y: ca. 100%. F. e. s. J. Roček, Coll. Czech. Chem. Communs. *19*, 275 (1954).

Lead oxide/calcium sulfate *$PbO/CaSO_4$*

Carbodiimides from thioureas RNHCSNHR → RN:C:NR

402.



7 g. bis-(m-acetylphenyl)thiourea, Tegoglätte (highly dispersed PbO), Ca-sulfate, and a little S in 400 cc. acetone kept 93 min. at 54° → crude bis-(m-acetylphenyl)carbodiimide. Y: 97%.—High dilution, low temp., and addition of some Ca-sulfate are advantageous for the prepn. of sensitive carbodiimides. F. e. s. S. Hünig, H. Lehmann, and G. Grimmer, A. *579*, 77 (1953).

Lead acetate *$(CH_3COO)_2Pb$*

Hydantoins from N-thiocarbonyldipeptides ○

s. *9*, 578

1,2,4-Triazines

s. *9*, 579

Lead nitrate *$Pb(NO_3)_3$*

Carboxylic acids from carboxylic acid thioamides C(:NH)SH → COOH

s. *8*, 568

Sodium hypochlorite *NaOCl*

Carbodiimides from thioureas RNHCSNHR → RN:C:NR

s. *7*, 538

Via intermediates *v.i.*

Isothiocyanates from amines NH_2 → N:C:S

s. *1*, 401; s. a. M. G. Ettlinger and J. E. Hodgkins, Am. Soc. *77*, 1831 (1955); silylmethyl isothiocyanates s. J. E. Noll, Am. Soc. *77*, 3149 (1955)

Carbon ↑ NC ⇑ C

Without additional reagents *w.a.r.*

α-Aminocarboxylic acids from carboxy(acylhydroxamates) via polypeptides ←

Lossen rearrangement

s. *8*, 569

Sodium hydride *NaH*

Rearrangement of Reissert compounds to o-acyl-N-heterocyclics ←

s. *9*, 580

Sodium hydroxide *NaOH*

Sec. from prim. amines and N-sulfonylcyanamides via sulfonylguanidines NH_2 → NHR

s. *6*, 529

Diazo compounds C:N
s. *10*, 606

Ureas from O-carbamylhydroxamates ·CONHOCONH· → ·NHCONH·

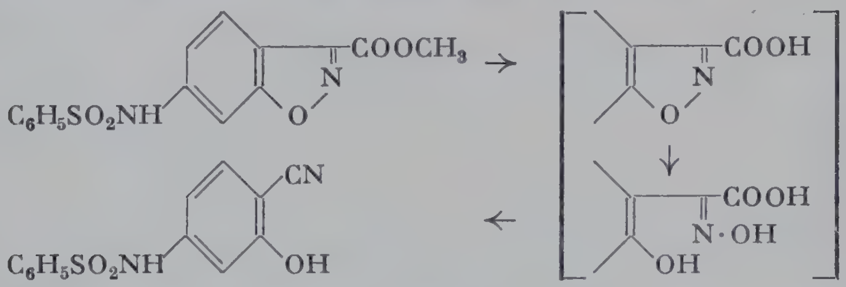
403. $C_6H_5CH_2CH_2CONHOCONHCH_2CH_2C_6H_5 \rightarrow C_6H_5CH_2CH_2NHCONHCH_2CH_2C_6H$

1.06 g. hydrocinnamo(phenethylcarbamylhydroxamic) acid dissolved in cold aq. NaOH, then heated 0.5 hr. at 100° → 0.82 g. *sym*-diphenethylurea. F. e. s. C. D. Hurd and L. Bauer, Am. Soc. *76*, 2791 (1954).

1-Subst. isoquinolines via 2-acyl-1,2-dihydroisoquinaldonitriles (Reissert compounds) ←
s. *7*, 818

o-Hydroxynitriles from 3-carbalkoxybenzisoxazoles C

404.



Methyl 6-(benzenesulfonamido)benzisoxazole-3-carboxylate heated in 2 *N* NaOH on a water bath until dissolved, allowed to cool, filtered, and the filtrate acidified by dropwise addition of concd. HCl → 4-(benzenesulfonamido)salicylonitrile. Y: 87%. F. e. s. W. Ried and H. Gutjahr, B. *86*, 1096 (1953).

Potassium hydroxide *KOH*

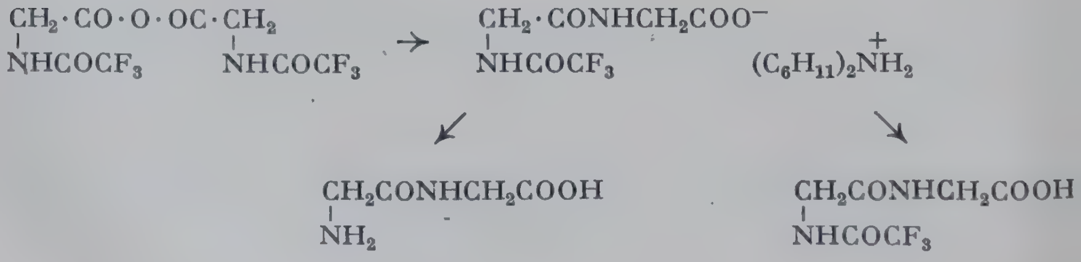
o-Alkyl-N-heterocyclics from Reissert compounds ←
s. *9*, 581; s. a. Am. Soc. *77*, 3128 (1955)

Diazo compounds from N-nitroso-N′-nitroguanidines $C:N_2$
s. *7*, 539

Dicyclohexylamine $(C_6H_{11})_2NH$

Peptides from trifluoroacetylaminocarboxylic acid anhydrides ←
Acids from their salts
Amines from trifluoroacetylamines
Protection of amino groups

405.



$$\underset{NHCOCF_3}{CH_2}\cdot CO\cdot O\cdot OC\cdot \underset{NHCOCF_3}{CH_2} \rightarrow \underset{NHCOCF_3}{CH_2}\cdot CONHCH_2COO^- \quad (C_6H_{11})_2\overset{+}{N}H_2$$

$$\swarrow \qquad \searrow$$

$$\underset{NH_2}{CH_2}CONHCH_2COOH \qquad \underset{NHCOCF_3}{CH_2}CONHCH_2COOH$$

A mixture of 1 mole dicyclohexylamine and abs. alcohol poured over N-trifluoroacetylglycine anhydride, and the product isolated after a short time → dicyclohexylammonium N-trifluoroacetylglycylglycinate (Y: 85%).

allowed to stand 30 min. with aq. NH_3 → glycylglycine (Y: 85%).	dissolved in water, and shaken 5 min. with Dowex-50 → N-trifluoroacetylglycylglycine (Y: 74%).

The N-trifluoroacetyl group can be easily removed in alkaline medium, e.g. with Dowex-2 (base) exchange resin, without hydrolysis of the peptide bond. F. Weygand and M. Reiher, B. *88*, 26 (1955).

Zinc *Zn*

Quinazolines ○
s. *6*, 530

Mercuric oxide *HgO*

Oximes from hydroxylamines ←
Labeled compounds s. *8*, 570

Acetic anhydride $(CH_3CO)_2O$

Nitriles from α-oximinocarboxylic acids $C(:NOH)COOH \rightarrow CN$
s. *6*, 823; *10*, 567

Buffer pH 4.6-4.8 ←

N-Condensed heterocyclics – Depolymerization ←
s. *8*, 571

Acetic acid CH_3COOH

Phthalazones from o-ketoacylhydrazones ○
s. *10*, 303

Thionyl chloride $SOCl_2$

Lactams
N-Subst. 2-pyrrolidones and 2-piperidines
s. *6*, 531

Ammonium benzenesulfonate $C_6H_5SO_3NH_4$

Pyrrolidines from tert-aminonitriles
s. *9*, 582

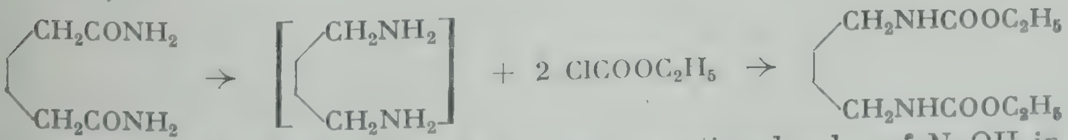
Sulfuric acid H_2SO_4

o-Alkyl-N-heterocyclics from Reissert compounds ←
s. *9*, 581

Alkali hypohalites ←

Hofmann degradation of carboxylic acid amides $CONH_2 \rightarrow NH_2$
3-Aminopyrazolones
s. *7*, 540

406.



$$(CH_2CONH_2)_2 \rightarrow [(CH_2NH_2)_2] + 2\ ClCOOC_2H_5 \rightarrow (CH_2NHCOOC_2H_5)_2$$

Urethans via amines. Liq. Br added to a stirred soln. of NaOH in ice-water, then adipamide added, heated 4 hrs. on a steam bath, then cooled in an ice-salt bath, and ethyl chloroformate added slowly → N,N'-dicarbethoxy-1,4-diaminobutane. Y: 96.5%. C. M. Samour and J. P. Mason, Am. Soc. *76*, 441 (1954).

Amines from nitriles via carboxylic acid amides CN → NH_2
s. *9*, 583

Amines from nitriles
s. *6*, 532

Aminocarboxylic acid esters from dicarboxylic acid imides C
s. *7*, 541

Hydrochloric acid *HCl*
Pyrrolidines from tert-aminonitriles ○
s. *9*, 582

Benzo-1,4-thiazine ring
s. *7*, 646

Via intermediates *v.i.*
4-Hydroxypyrrolidine-2-carboxylic acids ←
Halogenation
s. *9*, 584

Formation of Hal—Hal Bond

Uptake

Addition to Halogen HalHal ⇓ Hal

Sodium chloride *NaCl*
Sulfonium polyhalides ←
s. *9*, 585

Exchange

Halogen ↑ HalHal ⇅ Hal

Thionyl chloride *$SOCl_2$*
Chloroiodates ←
s. *6*, 533

Formation of Hal—S Bond

Exchange

Hydrogen ↑ HalS⇅H

Without additional reagents *w.a.r.*

Sulfenylhalides from mercaptans SH → SHal

s. 8, 572; sulfenylchlorides s. 8, 573; F. Kurzer and J. R. Powell, Org. Synth. 35, 99 (1955)

Sulfonic acid chlorides
from mercaptans and sulfinic acids SH ↘ SO_2Cl / SO_2H ↗
s. 8, 143

Oxygen ↑ HalS⇅O

Acetic acid *CH_3COOH*

Sulfenylbromides from sulfinic acids SO_2H → SBr

s. 6, 535; s. a. Soc. 1954, 90; 1955, 3798.

Phosphorus oxychloride *$POCl_3$*

Sulfonic acid chlorides
from potassium sulfonates SO_3K → SO_2Cl
s. 9, 586

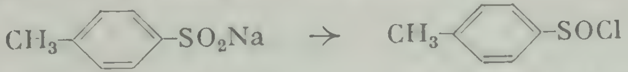
Phosphorus pentachloride *PCl_5*

from sodium sulfonates SO_3Na → SO_2Cl
s. 9, 392

Thionyl chloride *$SOCl_2$*

Sulfinic acid chlorides from sodium sulfinates SO_2Na → SOCl

07.



Na-p-toluenesulfinate dihydrate added portionwise at room temp. during 10-15 min. to excess $SOCl_2$, whereby the temp. rises at first and then drops to ca. 0°, te resulting mixture allowed to stand 1.5-2 hrs. at room temp. → p-toluenesulfinyl chloride. Y: 66-74%. F. Kurzer, Org. Synth. 34, 93 (1954).

Sulfonic acid chlorides from sulfonic acids SO_3H → SO_2Cl

s. 6, 536

Fluorosulfonic acid *FSO_3H*

Sulfonic acid fluorides from sodium sulfonates SO_3Na → SO_2F

s. 6, 590

Chlorosulfonic acid *$ClSO_3H$*

Sulfonic acid chlorides from alkali sulfonates SO_3^- → SO_2Cl

s. 6, 537; s. a. R. C. Shah, B. H. Shivjiani, and A. B. Kulkarni, J. Indian Chem. Soc., Ind. & News Ed. 17, 127, 131 (1954)

Nitrogen ↑ HalS⇅N

Sodium nitrite *$NaNO_2$*

Sulfonic acid fluorides from sulfonic acid amides $SO_2NH_2 \rightarrow SO_2F$
s. *7*, 543

Phosphorus oxychloride *$POCl_3$*

Sulfonic acid chlorides from sulfonylureas $SO_2NHCONHR \rightarrow SO_2Cl$
s. *8*, 574

Sulfur ↑ HalS⇅S

Without additional reagents *w.a.r.*

Sulfur trichlorides from disulfides $RSSR \rightarrow 2\,RSCl_3$
s. *9*, 587

Sulfonic acid chlorides from disulfides $RSSR \rightarrow 2\,RSO_2Cl$
s. *8*, 143

Fuming sulfuric acid *H_2SO_4,SO_3*

Sulfenylhalides from disulfides $RSSR \rightarrow 2\,RSCl$
s. *6*, 538

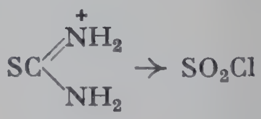
Carbon ↑ HalS⇅C

Without additional reagents *w.a.r.*

Anhydrous chlorination of thiocarboxylic acid esters and related compounds ←
s. *9*, 588

Chlorine *Cl*

Sulfonic acid chlorides from isothiouronium salts
s. *9*, 589



Formation of Hal—Rem Bond

Uptake

Addition to Remaining Elements HalRem⇓Rem

Without additional reagents *w.a.r.*

Selenium dihalides from selenides $>Se \rightarrow >SeHal_2$
s. *6*, 539

Exchange

Hydrogen ↑ HalRem⇅H

Without additional reagents *w.a.r.*

Halogenosilanes from silanes $SiH \rightarrow SiHal$
s. *6*, 540

Halogenophosphinic acid esters from phosphinic acid esters ←
s. *8*, 150

Triethylamine/polyhalogenalkanes	←
Chlorophosphoric acid esters and pyrophosphoric acid esters from dialkylphosphites s. *6*, 541	←

Oxygen ↑ HalRem ⇅ O

Without additional reagents	*w.a.r.*
Chloroboric acid esters s. *8*, 575	←
Halogeno- from alkoxy-silanes s. *9*, 590	SiOR → SiHal
Fluorosilanes s. *9*, 592	SiF
Chlorotitanium alkoxides s. *9*, 591	←
Sodium chloride	*NaCl*
Organomercuric chlorides from – acetates s. *9*, 712	HgOAc → HgCl
Phosphorus trichloride	*PCl_3*
Dichloroarsines from arsonic acids s. *7*, 544	AsO_3H_2 → $AsCl_2$
Phosphorus tribromide	*PBr_3*
Halogenosilanes and halides from alkoxysilanes s. *8*, 576	SiOR → SiHal
Phosphorus pentachloride	*PCl_5*
Phosphonic acid dichlorides from phosphonic acids s. *10*, 259	PO_3H_2 → $POCl_2$
Thionyl chloride	*$SOCl_2$*
Halogenosilanes from alkoxysilanes s. *8*, 577	SiOR → SiHal
Chlorophosphine oxides from phosphinic acids s. *7*, 671	R·POOH → R·POCl
Sulfur dioxide/iodine	*SO_2/I*
Dichloroarsines from arsonic acids s. *6*, 542	AsO_3H_2 → $AsCl_2$
Ammonium chloride	*NH_4Cl*
Halogenosilanes from silanols s. *8*, 700	SiOH → SiHal

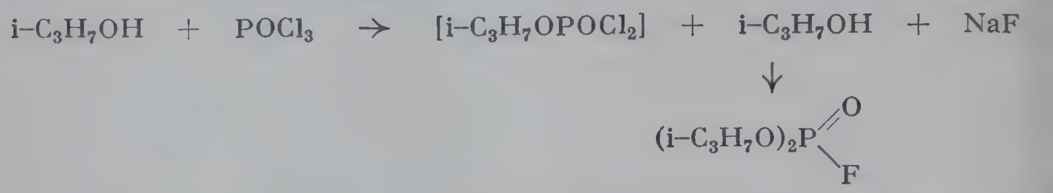
Halogen ↑ HalRem ⇅ Hal

Without additional reagents	*w.a.r.*
Fluorosilanes s. *9*, 592	SiF

Sodium fluoride *NaF*

Fluorophosphoric acid esters $(RO)_2P(O)F$

408.



38 cc. (0.5 mole) dry isopropanol added slowly at 30-35° to 46 cc. (0.5 mole) $POCl_3$ and CCl_4, next morning the diluent and HCl removed under reduced pressure below 50°, the resulting crude isopropyl dichlorophosphate added with stirring to a mixture of 42 cc. (0.55 mole) isopropanol and 75 g. (1.75 mole) NaF in dry benzene or CCl_4 at such a rate that the temp. is maintained at 45-50°, then refluxed 0.5 hr. with stirring → 55 g. diisopropyl fluorophosphate. F. methods s. A. H. Ford-Moore, L. J. Lermit, and C. Stratford, Soc. *1953*, 1776.

Aniline $C_6H_5NH_2$

Iodosilanes from chlorosilanes – Ruff reaction SiCl → SiI

s. *8*, 578

Aluminum iodide AlI_3

Siloxanes from fluorosilanes via iodosilanes ←

s. *6*, 543

Sulfur ↑ HalRem ⇅ S

Without additional reagents *w.a.r.*

Chlorothiophosphoric acid esters from dithiophosphoric acids $(RO)_2PSSH \rightarrow (RO)_2PSCl$

s. *6*, 156

Selenyltribromides and sulfenylbromides from selenylsulfides ←

s. *6*, 544

Silver salt Ag^+

Organosilicon compounds – Conversion series ←

Halogenosilanes from silthianes

s. *7*, 545

Sulfuryl chloride SO_2Cl_2

Chlorothiophosphoric acid esters from dithiophosphoric acid esters and bis(thionophosphonato) disulfides ←

s. *8*, 579

Chlorine *Cl*

Phosphoranetrioic trichlorides from dithiophosphinic acids $R_2PSSH \rightarrow R_2PCl_3$

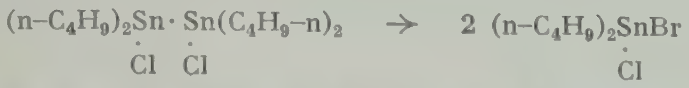
s. *10*, 700

Remaining Elements ↑ HalRem ⇅ Rem

Without additional reagents *w.a.r.*

Halogenostannanes from distannanes ←

09.



$$(n\text{-}C_4H_9)_2\underset{Cl}{Sn}\cdot\underset{Cl}{Sn}(C_4H_9\text{-}n)_2 \rightarrow 2\ (n\text{-}C_4H_9)_2\underset{Cl}{Sn}Br$$

A soln. of Br in CCl_4 added to a soln. of 1.2-dichlorotetra-n-butyldistannane (prepn. s. 494) in CCl_4 and heated gently on a steam bath until the bromine color disappears after ca. 10 min. → bromochlorodi-n-butylstannane. Y: 72%. O. H. Johnson and H. E. Fritz, J. Org. Chem. *19*, 74 (1954).

Selenylhalides from diselenides RSeSeR → 2 RSeHal
s. *7*, 546

Carbon ↑ HalRem ⇅ C

Without additional reagents *w.a.r.*

Cleavage of silanes to halogenosilanes SiR → SiHal
s. *9*, 593

Cleavage of germanes via halogenogermanes ←
s. *7*, 547

Germanium oxides from germanes via halogenogermanes ←
s. *8*, 580

Organotin compounds ←
s. *7*, 548

Halogenolead compounds, organo ←
s. *6*, 545

Aluminum iodide *AlI_3*

Iodosilanes by cleavage of silanes ←
s. *6*, 546

Phosgene *$COCl_2$*

Chlorophosphoric acid esters from phosphites $(RO)_3P \rightarrow (RO)_2P(O)Cl$

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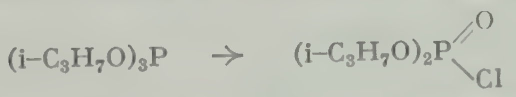


$$(i\text{-}C_3H_7O)_3P \rightarrow (i\text{-}C_3H_7O)_2P(=O)Cl$$

Triisopropyl phosphite stirred and treated at 30-35° with a fairly rapid stream of $COCl_2$ until after ca. 1 hr. rise of temp. and effervescence cease, then allowed to stand overnight → diisopropyl chlorophosphate. Y: 92%. F. e. s. A. H. Ford-Moore, L. J. Lermit, and C. Stratford, Soc. *1953*, 1776.

Hydrochloric acid *HCl*

Monoalkyl from dialkyl mercury compounds RHgR′ → RHgCl
s. *9*, 594

Elimination

Carbon ↑ **HalRem ⇑ C**

Aluminum chloride *$AlCl_3$*

Chlorosilanes from α-chloroalkylsilanes ←

411. $(CH_3)_3SiCHCl_2 \rightarrow (CH_3)_2SiCl_2 + CH_2{=}CH_2$

Dichloromethyltrimethylsilane added at first slowly and cautiously to anhydrous $AlCl_3$, addition continued more rapidly so as to maintain refluxing, occasionally heated with a Glas-Col mantle, stirred vigorously, and more catalyst added to avoid accumulation of unchanged startg. m., the product isolated after 6 hrs. → dimethyldichlorosilane. Y: 88%. F. e. s. L. H. Sommer et al., Am. Soc. *76*, 801 (1954).

Formation of Hal—C Bond

Uptake

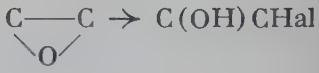
Addition to Oxygen and Carbon HalC ⇓ OC

Without additional reagents *w.a.r.*

Halogenoquinols from quinones ←
s. *9*, 595; s. a. A. P. Terent'ev, A. N. Grinev, and A. B. Terent'ev, Ж. *24*, 1433 (1954); C. A. *49*, 12353c

Halogenhydrins from cyclic ethers C
s. *7*, 549

Halogenhydrins from oxido compounds

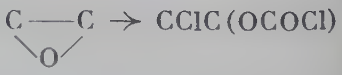


trans-Isomers s. *8*, 581

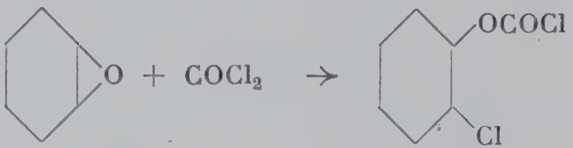
Walden inversion s. *6*, 547

Acoxyhalides from oxido compounds via halogenhydrins with rearrangement ←
s. *7*, 550

(α-Chloro)chloroformic acid esters from oxido compounds and phosgene

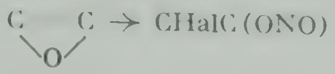


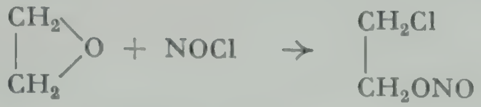
412.



Cyclohexene oxide added slowly with cooling to a small excess of phosgene in ethyl bromide, and allowed to stand overnight → o-chlorocyclohexyl chloroformate. Y: 75-80%. F. e. s. M. S. Malinovskii and N. M. Medyantseva, Ж. *23*, 221 (1953); C. A. *48*, 2580b.

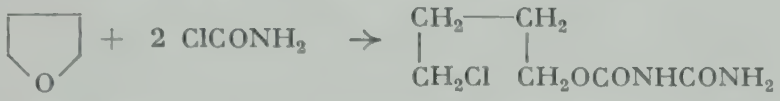
Halogenonitrous acid esters from oxido compounds



13. 

NOCl passed into a cooled mixture of ethylene oxide and ether until a red color results, then kept 24 hrs. at 0° → β-chloroethyl nitrite. Y: 72.5%. F. e. s. M. S. Malinkovskiĭ and N. M. Medvantseva, Ж. *23*, 84 (1953); C. A. *48*, 609i.

Tetrahydrofuran ring opening with acid chlorides

14. 

Carbamic acid chloride and tetrahydrofuran each precooled to 5-10°, mixed, the temp. kept below 30° by cooling, and the product isolated after 12-24 hrs. → 4-chloro-n-butylallophanate. Y: 50-60%. F. e. s. O. Moldenhauer and O. Trautmann, A. *580*, 172 (1953).

Halogenocarboxylic acids from lactones
s. *7*, 551

Halogenocarboxylic acid esters from lactones
with HBr s. *6*, 548; with HCl s. J. Baddiley and G. A. Jamieson, Soc. *1955*, 1085

Halogenolactols from oxidoketones and reverse reaction ←
Lactolides from lactols
Oxidoketones from halogenolactolides
s. *9*, 596

Sodium sulfate *Na_2SO_4*

1,1-Alkoxychlorides from aldehydes CHO → CHCl(OR)
s. *7*, 552

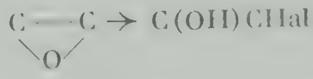
Potassium iodide/phosphoric acid *KI/H_3PO_4*
s. Phosphoric acid/potassium iodide

Magnesium bromide *$MgBr_2$*

Halogenocarboxylic acids from lactones
s. *6*, 549

Acetic acid *CH_3COOH*

Halogenhydrins from oxido compounds



s. *10*, 243; s. a. D. R. James, R. W. Rees, and C. W. Shoppee, Soc. *1955*, 1370

Halogenocarboxylic acids from lactones
s. *6*, 550

Phosphorus *P*

α,γ-Dibromocarboxylic acid bromides from γ-lactones
s. *6*, 569

Phosphoric acid/potassium iodide *H_3PO_4/KI*

Tetrahydrofuran ring opening
s. *6*, 584

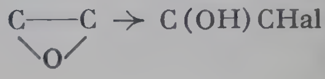
Phosphorus oxychloride/sulfuric acid *$POCl_3/H_2SO_4$*
s. *6*, 551

Sulfuric acid *H_2SO_4*

Dibromides from cyclic ethers
s. *9*, 597

Pyridine hydrochloride *C_5H_5N,HCl*

Halogenhydrins from oxido compounds
s. *9*, 598



Pyridinium ethiodide ←

Alkoxychlorohydrins by hydrogen chloride transfer ←
s. *8*, 582

Hydrochloric acid *HCl*

Oxazoline ring opening ⊂
s. *8*, 347

Addition to Nitrogen and Carbon HalC ⇓ NC

Without additional reagents *w.a.r.*

α-Halogenamines from azomethines ←
s. *10*, 677

Chloroarylenediamides from quinone diimides ←
s. *7*, 553

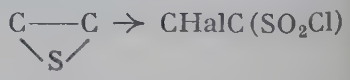
Halogenosulfonylaminophenols from quinone monoimides ←
s. *8*, 583

Halogenocyanamides from cyclic imines ⊂
s. *6*, 552; *9*, 599; s. a. H.-J. Nitzschke et al., B. *87*, 1635 (1954); *88*, 264 (1955)

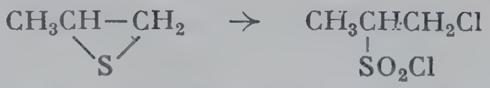
Addition to Sulfur and Carbon HalC ⇓ SC

Without additional reagents *w.a.r.*

2-Halogenosulfonic acid halides from ethylenesulfides



415.



$CH_3CH{-}CH_2$ (S) → $CH_3CH(SO_2Cl)CH_2Cl$

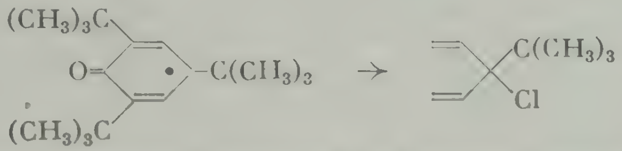
Propylene sulfide added dropwise at 0-12° below the surface of satd. Cl-water, while Cl is bubbled through the mixture so that an excess is always present, stirring continued 1 hr. in a slower Cl-stream, then air passed through to remove excess Cl → 1-chloro-2-propanesulfonyl chloride. Y: 70%. J. M. Stewart and H. P. Cordts, Am. Soc. 74, 5880 (1952).

Addition to Carbon Radicals HalC ⇓ C

Iodobenzene dichloride $C_6H_5ICl_2$

Reactions with radicals ←

16.



2,4,6-Tri-*tert*-butylphenoxyl dissolved in benzene under N_2, solid iodobenzene dichloride added, and warmed to 40° → 2,4,6-tri-*tert*-butyl-4-chlorocyclohexa-2,5-dien-1-one. Y: 91%. F. reactions s. E. Müller and K. Ley, B. 87, 922 (1954); cf. B. 87, 1605; Am. Soc. 75, 6242 (1953).

Addition to Carbon HalC ⇓ CC

Without additional reagents *w.a.r.*

Halides from ethylene derivatives C:C → CHCHal
s. *6*, 553; *8*, 584

Chlorides from ethylene derivatives with rearrangement ←
s. *6*, 554

β,γ-Ethylenehalides from dienes – 1,4-Addition ←
s. *8*, 585

1,2-Dihalides from ethylene derivatives C:C → CHalCHal
s. *6*, 555

Protection of a double bond
s. *6*, 280

1,2-Dibromides from ethylene derivatives C:C → CBrCBr
s. *8*, 84, 116; *9*, 899, 928

via quaternary ammonium bromide perbromides
s. *8*, 586

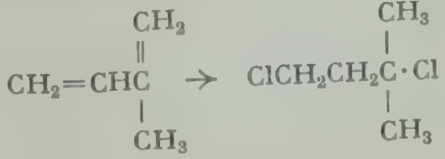
Mixed 1,2-dihalides from ethylene derivatives ←

7. $CF_2{=}CF_2 + ICl \rightarrow CF_2ClCF_2I$

Tetrafluoroethylene sealed with 10%-excess iodine monochloride in a Pyrex tube and slowly warmed to 50° → 1-chloro-2-iodo-tetrafluoroethane. Y: 94%.—Also bromoiodides with iodine monobromide s. R. N. Haszeldine, Soc. *1953*, 2075.

Dihalides by hydrohalogenation ←

8.



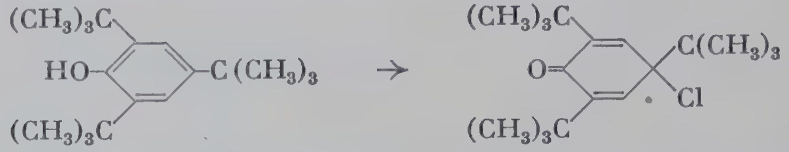
$$CH_2{=}CH\overset{\overset{CH_2}{\|}}{\underset{\underset{CH_3}{|}}{C}} \rightarrow ClCH_2CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\cdot Cl$$

Isoprene allowed to react with HCl at room temp. under an initia pressure of 30 atm. → 1,3-dichloro-3-methylbutane (startg. m. f. 544) Y: 86%. F. e. s. L. Schmerling and J. P. West, Am. Soc. *74*, 2885 (1952)

1,2-Nitrochlorides from ethylene derivatives C:C → CClC(NO$_2$
s. *6*, 558

4-Halogeno-2,5-cyclohexadienones from phenols ←

419.



Cl_2 introduced into a soln. of 2,4,6-tri-*tert*-butylphenol in glacial acetic acid with cooling and vigorous shaking → 2,4,6-tri-*tert*-butyl-4-chlorocyclohexa-2,5-dien-1-one. Y: 88%. E. Müller and K. Ley, B. *87*, 922 (1954).

2-Halogenacetals from enolethers via 1,2-dihalogenethers C:C(OR) → CHalC(OR)$_2$
s. *8*, 587

α-Iodoacetals from enol acetates C:C(OAc) → CIC(OR)$_2$
s. *9*, 600

1,1-Dialkoxy-1-chlorides from keteneacetals ←
s. *8*, 588

1,2-Dialkoxy-1,2-dihalides from enediolethers ←
s. *7*, 218

1,1,2-Trichlorides from ethylene derivatives via chlorohydrins and α,β-ethylenechlorides ←
s. *9*, 601

α-Halogenocarboxylic acid esters from keteneacetals ←
s. *8*, 589

Chlorination of quinonebetaines ←
s. *8*, 590

Halogenophthalides from ethylenecarboxylic acids ○
s. *8*, 591

Cyclopropane ring opening
Halogenosteroids from 3,5-cyclosteroids
s. *9*, 635; cyclopropane ring opening s. a. G. Laber, A. *588*, 79 (1954)

Irradiation ←

Bromides from ethylene derivatives C:C → CHCBr
Free radical additions
s. *9*, 602

1,2-Dihalides from ethylene derivatives C:C → CHalCHal
s. *6*, 556

Ethylene from acetylene derivatives via 1,2-dibromides ←
Deutero compounds s. *9*, 603

Irradiation/acetamide s. Acetamide/irradiation

Sodium acetate *CH_3COONa*

1,2-Dibromides from ethylene derivatives C:C → CBrCBr
s. *9*, 362

Potassium iodide/phosphoric acid *KI/H_3PO_4*
s. Phosphoric acid/potassium iodide

Magnesium oxide *MgO*

1,2-Alkoxyhalides from ethylene derivatives C:C → C(OR)CHal
s. *9*, 604

Aluminum halide *$AlHal_3$*

Addition of hydrogen halides to acetylene derivatives ←
s. *9*, 605

Acetamide/irradiation ←

1,2-Dibromides from ethylene derivatives C:C → CBrCBr

420. $(CF_3)_2C{=}CF_2 \rightarrow (CF_3)_2CBrCF_2Br$

A mixture of perfluoroisobutene (prepn. s. 563), Br_2, a little acetamide, and 3 drops of water irradiated 3 hrs. with an UV-lamp → perfluoroisobutene dibromide. Y: 35%.—Bromination in the absence of acetamide was unsuccessful. T. J. Brice et al., Am. Soc. 75, 2698 (1953).

tert-Butyl peroxide *$(CH_3)_3C{\cdot}OO{\cdot}C(CH_3)_3$*

ω-Bromoalkanols from ω-ethylenealkanols via boric acid esters – Masking of hydroxyl groups ←

21.

$$\begin{array}{rcl} 3\ CH_2{=}CH[CH_2]_8CH_2OH + H_3BO_3 & \rightarrow & \left[\begin{array}{c}(CH_2{=}CH[CH_2]_8CH_2O)_3B\\ \downarrow\\ (BrCH_2CH_2[CH_2]_8CH_2O)_3B\end{array}\right]\\ 3\ BrCH_2CH_2[CH_2]_8CH_2OH & \leftarrow & \end{array}$$

A mixture of 10-undecenol, boric acid, and toluene refluxed 2 hrs. with separation of the water formed, *tert*-butyl-peroxide added, then dry HBr introduced at 0-2° during ca. 6 hrs. while more peroxide is added, allowed to stand overnight in a refrigerator, part of the toluene distilled off in vacuo at 35-40°, and the residue stirred 1 hr. with water at 50° → 11-bromo-1-undecanol (startg. m. f. 143). Y: 69%.—Masking of the free hydroxyl group is necessary because it seems to act as an antioxidant. F. e. s. M. G. J. Beets and W. Meerburg, R. 72, 411 (1953).

Benzoyl peroxide *$(C_6H_5COO)_2$*

Deuterohalides from ethylene derivatives ←
s. *8*, 592

Acetic acid CH_3CO

Halides from ethylene derivatives C:C → CHC

Bromides s. *10*, 679; chlorides s. M. Stoll, Helv. *38*, 1587 (1955)

N-Bromoacetamide CH_3CONH

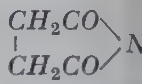
Bromohydrins from ethylene derivatives C:C → C(OH)C

Labeled compounds s. *7*, 554

1,2-Chlorobromides from ethylene derivatives C:C → CClC

s. *7*, 555

N-Bromosuccinimide

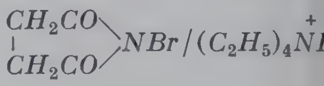


$\begin{array}{l}CH_2CO\\ CH_2CO\end{array} > N$

Halogenhydrins from ethylene derivatives C:C → C(OH)C

s. *8*, 272; s. a. C. O. Guss and R. Rosenthal, Am. Soc. *77*, 2549 (195

N-Bromosuccinimide/tetraethylammonium bromide



$\begin{array}{l}CH_2CO\\ CH_2CO\end{array} > NBr/(C_2H_5)_4\overset{+}{N}$

Reaction between ethylene derivatives and N-bromosuccinimide

s. *9*, 606

Amyl nitrite RO

α-Nitrosohalides from ethylene derivatives C:C → C(NO)C

s. *7*, 240

Nitrosyl chloride NC

Reaction of nitrosyl chloride with ethylene derivatives

1,2-Nitrochlorides and 1,2-dihalides

s. *6*, 558

Phosphoric acid/potassium iodide H_3PO_4/

Iodides from ethylene derivatives C:C → CH

s. *6*, 584

Antimony trichloride Sb

1,2-Dichlorides from ethylene derivatives C:C → CClC

cis-trans-Isomers

s. *6*, 556

Antimony pentachloride Sb

Stereospecificity

s. *7*, 738

Sulfuryl chloride SO_2

Halogenolactones

Lactones from halogenocarboxylic acid esters with simultaneous replacement of carbalkoxy groups by hydrogen

Trihalides from ethylene derivatives

s. *9*, 607

Chromyl chloride CrO_2Cl_2

Chlorohydrins from ethylene derivatives $C{:}C \rightarrow C(OH)CCl$

s. *7*, 557

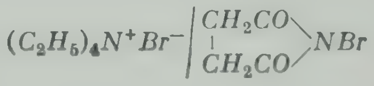
tert-Butyl hypochlorite $(CH_3)_3C{\cdot}OCl$

in acetic acid s. *2*, 488; in acetone-water s. J. Kebrle and P. Karrer, Helv. *37*, 484 (1954)

Calcium hypochlorite $Ca(OCl)_2$

s. *6*, 557

Tetraethylammonium bromide/N-bromosuccinimide s. N-bromosuccinimide/tetraethylammonium bromide



$(C_2H_5)_4N^+Br^- \left| \begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array} \right\rangle NBr$

Pyridine hydrobromide perbromide $C_5H_5N,HBr{\cdot}Br_2$

1,2-Dibromo-3-alcohols from 2-ethylenealcohols $C{:}C \rightarrow CBrCBr$

s. *9*, 608

Ferric chloride $FeCl_3$

1,2-Dichlorides from ethylene derivatives $C{:}C \rightarrow CClCCl$

s. *8*, 593

Via intermediates *v.i.*

1,2-Alkoxyhalides from ethylene derivatives via monoalkylmercury compounds $C{:}C \rightarrow C(OR)CHal$

s. *8*, 594

Rearrangement

Hydrogen/Carbon Type HalC ↶ HC

Sodium acetate CH_3COONa

Change in configuration of halogenosteroids ←

s. *9*, 609

Hydrobromic acid HBr

Bromination with migration of bromine ←

s. *6*, 559; migration of bromine s. a. A. C. B. Smith and W. Wilson, Soc. *1955*, 1342

Exchange

Hydrogen ↾ HalC ⇅ H

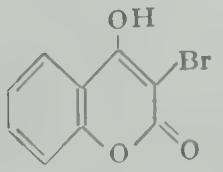
Without additional reagents *w.a.r.*

Chlorination in aqueous suspension H → Cl

s. *7*, 572

Bromination H → Br

22.



Br added dropwise to an ice-cold soln. of 4-hydroxycoumarin in abs. *ethanol*, after allowing the reaction to proceed for 0.5 hr. the soln. added dropwise with vigorous stirring to ice-water, and kept at room temp. overnight → 3-bromo-4-hydroxycoumarin. Y: 96%. H. R. Eisenhauer and K. P. Link, Am. Soc. *76*, 1647 (1954).

s. a. *6*, 560; *8*, 595, 943

with bromine vapor

CO_2 as carrier s. *3*, 154; N_2 as carrier s. D. R. Howton, J. F. Mead, and W. G. Clark, Am. Soc. *77*, 2896 (1955)

Migration of bromine

s. *6*, 559

α,β-Ethylenebromides from ethylene derivatives
Reaction of bromine vapor with solid compounds

s. *6*, 562

β,γ-Ethylenebromides from ethylene derivatives

s. *7*, 558

α-Dihalogenoketones from ketones $COCH_2 \rightarrow COCHal_2$

α-Dichloroketones s. *3*, 430; α-dibromoketones s. J. J. Klingenberg, Org. Synth. *35*, 11 (1955)

1,1-Acoxyhalides from acoxy compounds $CH(OAc) \rightarrow CBr(OAc)$

s. *7*, 344

α-Bromoacetals from aldehydes $CH \cdot CHO \rightarrow CBr \cdot C(OR)_2$

423. $(CH_3CHO)_3 \rightarrow BrCH_2CH(OC_2H_5)_2$

Br added dropwise during ca. 5 hrs. with vigorous stirring to a cold soln. of paraldehyde in ethanol → bromoacetaldehyde diethylacetal. Y: 72.5%. F. e. s. H. Baganz, K.-H. Dossow, and W. Hohmann, B. *86*, 148 (1953); in ether containing peroxide s. G. Darzens and M. Meyer, C. r. *236*, 292 (1953).

α-Bromo-β-diketones from 3-keto-1,2-en-1-ols ←

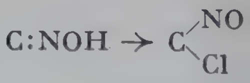
s. *8*, 596

Halogenofuranones from acoxyfurans ←

s. *9*, 610

1,1-Nitrosochlorides from oximes

s. *10*, 2



$$C{:}NOH \rightarrow C\begin{smallmatrix}NO\\Cl\end{smallmatrix}$$

Aliphatic nitrohalides from nitro compounds $H \rightarrow Hal$

s. *6*, 561

Irradiation ←

Photohalogenation of aliphatic compounds in the vapor phase
Directed halogenation

Photochlorination s. *9*, 611; photobromination s. M. S. Kharasch, W. S. Zimmt, and W. Nudenberg, J. Org. Chem. *20*, 1430 (1955)

Chlorination H → Cl

s. *8*, 213; polyfluoro compounds s. R. N. Haszeldine et al., Soc. *1955*, 3005, 3880

1,1,1-Trichlorides $CH_3 \rightarrow CCl_3$

s. *10*, 451

Bromination H → Br

s. *9*, 972; *10*, 163

Potassium hydroxide *KOH*

1,1-Nitrohalides from aliphatic nitro compounds H → Hal

Halogenonitrosulfonic acids

s. *8*, 597

Sodium/alcohol *NaOR*

s. *8*, 932

Sodium acetate CH_3COONa

1,1,1-Trihalides $CH_3 \rightarrow CHal_3$

s. *7*, 560

Sodium acetate/phosphoric acid CH_3COONa/H_3PO_4

s. Phosphoric acid/sodium acetate

Potassium bromide *KBr*

Bromination H → Br

424. Bromine in aq. ca. 15%-KBr soln. added slowly with shaking to a soln. of 2.61 g. 2-naphthyl tetraacetyl-β-D-glucoside in acetic acid until the Br-color persists → 2.64 g. 1-bromo-2-naphthyl tetraacetyl-β-D-glucoside.—A Br soln. in acetic acid gave a yield of only 25%. W. A. Bonner, M. J. Kubitshek, and R. W. Drisko, Am. Soc. *74*, 5082 (1952).

s. a. *7*, 561

Sodium iodide/ammonia NaI/NH_3

Iodination H → I

s. *8*, 598

Potassium iodide *KI*

s. *9*, 612

Potassium iodide/sodium hydroxide *KI/NaOH*

s. *9*, 613

Potassium iodide/prim. amines KI/RNH_2

s. *6*, 563

Sodium salt Na^+

β-Iodo-α,γ-diketocarboxylic acid esters from α,γ-diketocarboxylic acid esters

s. *10*, 162

Pyridine C_5H_5N

Bromination H → Br

s. *6*, 564

Silver trifluoroacetate *CF_3COOAg*

Halogenation – Halogen cations H → Hal
s. *7*, 562

Silver sulfate *Ag_2SO_4*

Bromination
s. *7*, 563

Iodination
s. *7*, 564

Silver salt *Ag^+*
s. *7*, 565 H → Hal

Calcium carbonate *$CaCO_3$*

α-Oxobromides from oxo compounds H → Br
α-Bromoaldehydes s. *5*, 650; α-bromoketones s. A. C. B. Smith and W. Wilson, Soc. *1955*, 1342

Ethylmagnesium bromide *C_2H_5MgBr*

Replacement of active hydrogen by iodine H → I
s. *10*, 453

Mercuric oxide *HgO*

Iodination
s. *9*, 614; in CCl_4 containing acetic anhydride s. F. G. Baddar, H. A. Fahim, and A. M. Fleifel, Soc. *1955*, 3302

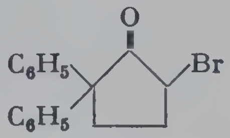
Mercuric chloride *$HgCl_2$*

Iodolactones from ethylenecarboxylic acids
s. *10*, 426

Ether *$(C_2H_5)_2O$*

Bromination H → Br

425.



Br/ether complex (prepared by slow addition of dry ether to ice cold Br until a second layer is formed) dropped into a stirred soln. of 2,2-diphenylcyclopentanone (prepn. s. 561) in dry ether during 15 min. at room temp. → 5-bromo-2,2-diphenylcyclopentanone. Y: 76%.—A more highly brominated by-product was formed by other methods. N. R. Easton and S. J. Nelson, Am. Soc. *75*, 640 (1953).

Dioxane ←
s. *9*, 615; s. a. A. P. Terent'ev, L. J. Belen'kiĭ, and L. A. Yanovskaya, Ж. *24*, 1265 (1954); C. A. *49*, 12327d

Peroxides ←

α-Bromoacetals from aldehydes CH·CHO → CBr·C(OR)$_2$
s. *10*, 423

Acetic acid *CH_3COOH*

α,β-Ethylenehalides from ethylene derivatives H → Hal
s. *8*, 599

Selective bromination
s. *8*, 600

H → Br

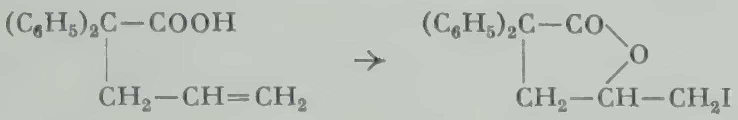
Cyanogen iodide

ICN

Iodolactones from ethylenecarboxylic acids

←

426.



A soln. of ICN in chloroform added to a soln. of 2,2-diphenylpenten-4-oic acid in the same solvent, and kept 7 days in a refrigerator → 2,2-diphenyl-5-iodo-4-pentanolactone. Y: 82%.—A less pure product is obtained with iodine in the presence of $HgCl_2$. F. e., with lower yields, and limitations s. R. T. Arnold and K. L. Lindsay, Am. Soc. *75*, 1048 (1953).

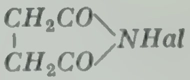
N-Chlorodiethylamine

$(C_2H_5)_2NCl$

Halogenation
s. *10*, 471

H → Hal

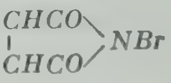
N-Halogenosuccinimide



$$\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \!\!> NHal$$

Halogenation
Azulenes s. *9*, 616

N-Bromosuccinimide



$$\begin{matrix} CHCO \\ | \\ CHCO \end{matrix} \!\!> NBr$$

Bromination

H → Br

s. *6*, 565, 840; *8*, 159; *9*, 927; of N-heterocyclics s. *9*, 640; s. a. R. Adams and I. J. Pachter, Am. Soc. *76*, 1845 (1954)

Directed bromination
s. *9*, 611

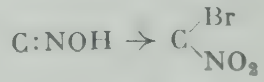
α-Bromoacetals from acetals
s. *7*, 566

α-Bromoketones from sec. alcohols

←

β-Bromo-α-ketocarboxylic acid esters
s. *10*, 227

1,1-Nitrobromides from oximes
s. *9*, 168

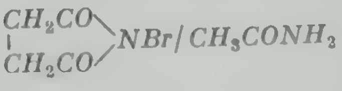


$$C{:}NOH \rightarrow C\begin{matrix} Br \\ NO_2 \end{matrix}$$

H → Br

Bromination with simultaneous formation of sym. disulfides from mercaptans
s. *8*, 601

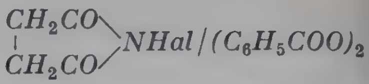
N-Bromosuccinimide/acetamide



$$\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \!\!> NBr/CH_3CONH_2$$

Bromination of sensitive compounds
s. *7*, 785

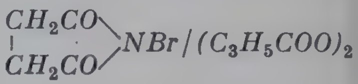
N-Halogenosuccinimide/benzoyl peroxide


$\begin{matrix}CH_2CO\\ CH_2CO\end{matrix}\!>NHal/(C_6H_5COO)_2$

Halogenation of satd. compounds H → Hal

427. A mixture of cyclohexane, N-chlorosuccinimide, and CCl_4 refluxed 12 hrs. with a little benzoyl peroxide → cyclohexyl chloride. Y: 42%.— Methylene groups are more readily attacked than methyl groups. F. e. s. Ng. Ph. Buu-Hoï and P. Demerseman, J. Org. Chem. *18*, 649 (1953).

N-Bromosuccinimide/benzoyl peroxide

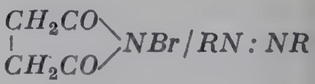

$\begin{matrix}CH_2CO\\ CH_2CO\end{matrix}\!>NBr/(C_3H_5COO)_2$

Bromination H → Br
s. *8*, 349

of heterocyclics
Isosters s. *6*, 566

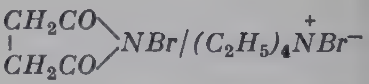
of unsatd. compounds
in the allyl position with rearrangement
s. *6*, 567

N-Bromosuccinimide/aliphatic azo compounds


$\begin{matrix}CH_2CO\\ CH_2CO\end{matrix}\!>NBr/RN:NR$

with radical forming catalysts
s. *8*, 604

N-Bromosuccinimide/tetraethylammonium bromide


$\begin{matrix}CH_2CO\\ CH_2CO\end{matrix}\!>NBr/(C_2H_5)_4\overset{+}{N}Br^-$

Reaction between ethylene derivatives and N-bromosuccinimide ←
s. *9*, 606

Nitric acid HNO_3

Iodination H → I
s. *6*, 568; in acetic acid-H_2SO_4 s. A. N. Novikov, Ж. *24*, 655 (1954); C. A. *49*, 5338a

Phosphorus *P*

α,α-Dihalogenoketones from ketones $CH_2CO \rightarrow CBr_2CO$
s. *8*, 602

Halogenation, also with 2-piperidone ring closure H → Hal
s. *7*, 567

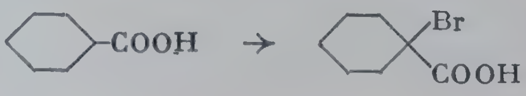
α-Bromo-γ-lactones from γ-lactones via α,β-dibromocarboxylic acid bromides H → B
s. *6*, 569

Phosphorus/sulfuryl chloride s. Sulfuryl chloride/phosphorus P/SO_2Cl_2

Polyphosphoric acid $H(PO_3)_xOH$

α-Bromocarboxylic acids from carboxylic acids

428.



A mixture of cyclohexanecarboxylic acid and polyphosphoric acid heated 10 min. at 120° with stirring, then bromine added dropwise, heating and stirring continued for 4 hrs., water added dropwise, and excess bromine removed in vacuo → α-bromocyclohexanecarboxylic acid. Y: 76.5%. F. e. s. E. E. Smissman, Am. Soc. *76*, 5805 (1954).

Phosphoric acid/sodium acetate *H_3PO_4/CH_3COONa*

Bromination of acid-sensitive compounds
s. *6*, 570

Phosphorus trichloride *PCl_3*

α-Halogenocarboxylic acids from carboxylic acids H → Hal
s. *10*, 680

Phosphorus tribromide *PBr_3*

α-Halogenocarboxylic acid esters from carboxylic acids

429. $n\text{-}C_{10}H_{21}CH_2COOH \rightarrow [n\text{-}C_{10}H_{21}CHBrCOBr] \rightarrow n\text{-}C_{10}H_{21}CHBrCOOCH_3$

1.05 equivalents of Br_2 added rapidly to a stirred mixture of dodecanoic acid and 1.05 equivalents of PBr_3, which is thereby converted into PBr_5, then an additional 1.1 equivalents of Br_2 added during ca. 15 min., heated 4 hrs. with stirring, cooled to room temp., methanol added, stirred 30 min. at room temp. and 1 hr. under reflux → methyl 2-bromododecanoate. Y: 90-95%.—This procedure is most convenient for the prepn. of small lots. J. Cason, N. L. Allinger, and G. Sumrell, J. Org. Chem. *18*, 850 (1953).

Phosphorus pentachloride *PCl_5*

1-Chloro-2-trichloroacetylsugars ←
s. 8, 18

Antimony pentachloride *$SbCl_5$*

Halogenation H → Hal
s. *6*, 571

Hydrogen peroxide *H_2O_2*

Iodination H → I
s. 8, 603

Hydrogen peroxide/hydrochloric acid *H_2O_2/HCl*

Halogenation with position shift ←
s. 7, 568; migration of halogen s. a. R. *72*, 853 (1953)

Thionyl chloride *$SOCl_2$*

Chlorination H → Cl
s. 7, 569

Sulfuryl chloride *SO_2Cl_2*

Halogenation H → Hal
s. *9*, 584

Chlorination H → Cl
s. *6*, 572

α-Chloroketones from ketones
s. *1*, 417; s. a. M. Kopp, Bl. *1954*, 628

α-Chlorocarboxylic acids from dicarboxylic acids via α-chloro-α-dicarboxylic acids
s. *7*, 570

α-Chloro-β-ketocarboxylic acid esters from β-ketocarboxylic acid esters
s. *6*, 573

Trihalides from ethylene derivatives ←
s. *9*, 607

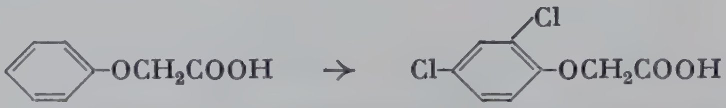
Sulfuryl chloride/aliphatic azo compounds $SO_2Cl_2/RN{:}NR$

Halogenation with radical forming catalysts H → Hal
s. *8*, 604

Sulfuryl chloride/acetic acid SO_2Cl_2/CH_3COOH

Chlorination H → Cl

430.



The temp. of a mixture of phenoxyacetic acid, excess SO_2Cl_2, and glacial acetic acid slowly raised from 0 to 75°, then maintained at the latter temp. until gas evolution ceases → 2,4-dichlorophenoxyacetic acid. Y: 74%.—In the absence of a solvent, only the p-chloro derivative is obtained and no reaction occurs in boiling CCl_4. When Cl_2 is used, regulation of the quantity is troublesome on a small scale. M. Fields, S. Rothchild, and M. A. Leaffer, Am. Soc. *74*, 2435 (1952).

Sulfuryl chloride/phosphorus SO_2Cl_2/P

also with 2-piperidone ring closure
s. *7*, 567

Sulfuric acid H_2SO_4

Bromination H → Br
s. *8*, 512

p-Toluenesulfonic acid *TsOH*
s. *9*, 968

tert-Butyl hypochlorite $(CH_3)_3C{\cdot}OCl$

Chlorination of phenols H → Cl
s. *8*, 605

Ketones from sec. alcohols with subsequent chlorination CH(OH)CH → COCCl
s. *9*, 617

Oxidation-chlorination
α-Chloroketones from sec. alcohols
s. *9*, 618

Carboxylic acid chlorides from aldehydes CHO → COCl
s. 7, 571

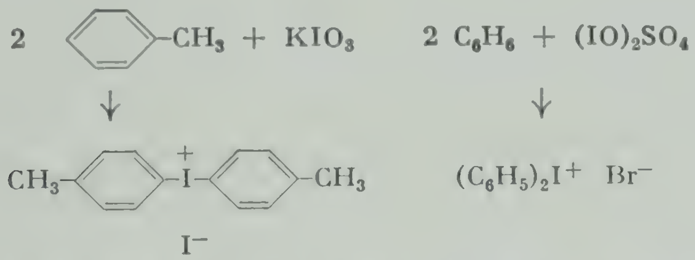
Iodyl sulfate $(IO)_2SO_4$
Sym. iodonium salts R_2I^+
s. 10, 431

Alkali hypohalites ←
Halogenoacetylenes C:CH → C:CHal
Bromoacetylenes s. 4, 494; also chloroacetylenes s. W. M. McLamore, S. Y. P'An, and A. Bavley, J. Org. Chem. 20, 109 (1955)

Sodium hypochlorite *NaOCl*
Chlorination H → Cl
s. 7, 572

Potassium iodate KIO_3
Sym. iodonium salts R_2I^+

431.



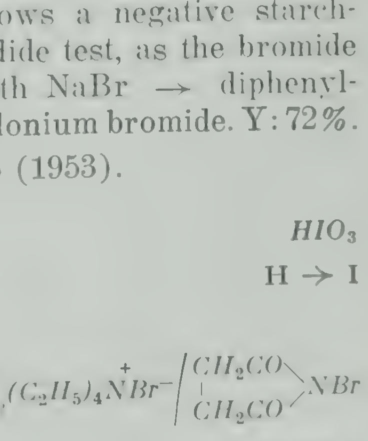
A soln. of H_2SO_4 and actic acid added below 3° to a well stirred mixture of toluene, K-iodate, acetic acid, and acetic anhydride, stirring continued 3 hrs. in the ice bath then overnight until the mixture shows a negative starch-iodide test. and the product isolated as the iodide with KI → 4,4'-dimethylphenyl-iodonium iodide. Y: 91%.

Acetic anhydride, then benzene added below 10° to a stirred suspension of iodyl sulfate in H_2SO_4, and the product isolated after 2 hrs., when the mixture shows a negative starch-iodide test, as the bromide with NaBr → diphenyliodonium bromide. Y: 72%.

F. e. s. F. M. Beringer et al., Am. Soc. 75, 2705 (1953).

Iodic acid HIO_3
Iodination H → I
s. 8, 545

Tetraethylammonium bromide/N-bromosuccinimide
s. *N-Bromosuccinimide/tetraethylammonium bromide*



$(C_2H_5)_4\overset{+}{N}Br^- \Big| \begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} > NBr$

Pyridine perbromide $C_5H_5N{\cdot}Br_2$
1,1-Dibromides from bromides CHBr → CBr_2
s. 8, 606

Hydrochloric acid *HCl*

Chlorination H → Cl
s. *7*, 573

α-Bromoketones from ketones H → Br
s. *7*, 574

Hydrobromic acid *HBr*

Bromination

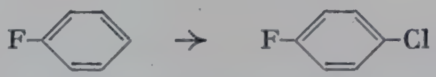
Halogenospirostanes
s. *7*, 575

of ketones
s. *2*, 494; *3*, 373; *4*, 495; s. a. R. H. Burnell and W. I. Taylor, Soc. *1954*, 3486

Ferric chloride *$FeCl_3$*

Chlorination H → Cl
s. *7*, 576

432.



Directed chlorination. Fluorobenzene heated 4 hrs. with 0.5 mole $FeCl_3$ at 145-153° in a nickel bomb → crude p-chlorofluorobenzene. Y: 80%. F. e. s. P. Kovacic and N. O. Brace, Am. Soc. *76*, 5491 (1954).

Cobalt fluoride *CoF_3*

Fluorination H → F
s. *7*, 577

Via intermediates *v.i.*

α-Bromoaldehydes from aldehydes – General method H → Br
α-Bromoacetals from enol acetates via α,β-bromoacetates
s. *6*, 575

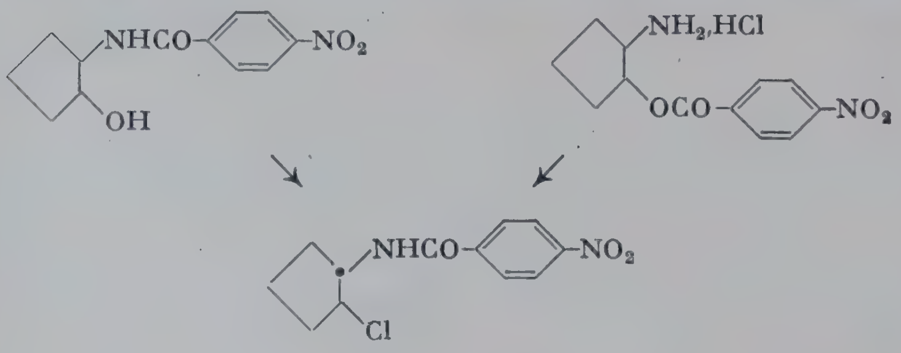
5-Bromo-2,3-dihydropyrans
s. *9*, 619

Oxygen ↑ HalC ⇅ O

Without additional reagents *w.a.r.*

Replacement of hydroxyl by halogen with cis-trans-rearrangement
trans-2-Acylaminohalides from cis-2-acoxyamine hydrochlorides

433.



A soln. of *cis*-2-nitrobenzamidocyclopentanol in dry dioxane satd. with HCl gas, and gently refluxed for 3 hrs. →	A suspension of *cis*-2-aminocyclopentyl p-nitrobenzoate hydrochloride in dry dioxane refluxed 3 hrs. →
d,l-*trans*-N-p-nitrobenzoyl-2-chlorocyclopentylamine	
Y: 62%	Y: 50%

E. E. van Tamelen, Am. Soc. *74*, 2074 (1952).

Dihalides from diols and cyclic ethers
s. *8*, 607

α,ω-Diiodides
s. *8*, 608

Halides from ethers OR → Hal
s. *10*, 16

Halogenamines from aminoethers
s. *7*, 529

1,1-Alkoxyhalides from acetals $C(OR)_2 \rightarrow C(OR)Hal$
s. *9*, 620

Replacement of acoxy groups by bromine OAc → Br
s. *6*, 731

Acetochlorosugars OAc → C
s. *8*, 609

Acetobromosugars with liquid hydrogen bromide OAc → Br
s. *9*, 621

Alcohols from glycols via diacoxy compounds, halogenhydrins, and oxido compounds ←
Optically active compounds s. *7*, 579

Halides from boric acid esters ←
Optically active compounds s. *8*, 610

Dihalides from cyclic ethers C
s. *7*, 549; *8*, 607

Alkali halides ←
Halides from p-toluenesulfonic acid esters OTs → Hal
s. *9*, 622; s. a. G. V. D. Tiers, H. A. Brown, and T. S. Reid, Am. Soc. *75*, 5978 (1953); fluorides with KF s. W. F. Edgell and L. Parts, Am. Soc. *77*, 4899, 5515 (1955)

Alkali bromide/sulfuric acid s. Sulfuric acid/alkali bromide

Sodium bromide *NaBr*
Replacement of hydroxyl by bromine via p-toluenesulfonic acid esters OH → Br
s. *9*, 623

Sodium iodide NaI

Iodides from sulfonates of carbohydrates $OSO_2R \rightarrow I$

s. *6*, 576; of glycals s. *6*, 577

Iodides from p-toluenesulfonic acid esters OTs → I

s. *9*, 624

Sodium iodide/sodium hydrogen carbonate $NaI/NaHCO_3$

s. *7*, 580

Potassium iodide/phosphoric acid KI/H_3PO_4

s. Phosphoric acid/potassium iodide

Triethylamine/phosphorus oxychloride $(C_2H_5)_3N/POCl_3$

Replacement of hydroxyl by chlorine OH → Cl

Exchange of substituents of amines

s. *9*, 625

Dimethylaniline/phosphorus oxychloride $C_6H_5N(CH_3)_2/POCl_3$

Chlorides from hydroxy compounds

s. *2*, 502; *3*, 457; s. a. A. Bendich, P. J. Russell, Jr., and J. J. Fox, Am. Soc. *76*, 6073 (1954)

Halogeno- from oxo-N-heterocyclics ←

s. *8*, 611

Dimetylaniline/thionyl chloride $C_6H_5N(CH_3)_2/SOCl_2$

Halides from alcohols OH → Hal

s. *8*, 612; *9*, 108

Pyridine/borone trichloride C_5H_5N/BCl_3

Halides from alcohols and ethers ←

Optically active compounds s. *8*, 152

Pyridine/thionyl chloride $C_5H_5N/SOCl_2$

Halogenoketones from hydroxyketones OH → Hal

s. *9*, 626

Subst. carboxylic acid amides from carboxylic acids via carboxylic acid chlorides $COOH \rightarrow CON\langle$

s. *9*, 627

Pyridine/benzenesulfonyl chloride $C_5H_5N/C_6H_5SO_2Cl$

Carboxylic acid chlorides from carboxylic acids COOH → COCl

s. *6*, 578

Lutidine/phosphorus oxychloride ←

α-Halogeno- from α-hydroxy-nitriles OH → Hal

s. *6*, 579

Calcium carbonate/phosphorus pentachloride $CaCO_3/PCl_5$

Halogeno- from hydroxy- and 3,5-cyclo-steroids ←

Epimerization

s. *9*, 635

Calcium carbonate/thionyl chloride $CaCO_3/SOCl_2$

Partial replacement of hydroxyl by chlorine OH → Cl

s. *6*, 580

Calcium chloride $CaCl_2$

Chlorides from alcohols
s. *6*, 812

Calcium bromide $CaBr_2$

Bromides from tosylates OTs → Br
s. *7*, 581

Zinc chloride/acetyl chloride $ZnCl_2/CH_3COCl$
s. Acetyl chloride/zinc chloride

Zinc chloride/hydrochloric acid $ZnCl_2/HCl$

Ethylenechlorides from alicyclic alcohols

s. *8*, 613

Boron trichloride BCl_3

Cleavage of mixed ethers ROR′ → RCl
s. *9*, 194

Boron trichloride/pyridine s. Pyridine/boron trichloride BCl_3/C_5H_5N

Acetic anhydride $(CH_3CO)_2O$

Bromides from ethers OR → Br
Long chain α,ω-dihalides s. *9*, 628

Acetic acid CH_3COOH

Acylhalogenosugars OAc → Hal
s. *8*, 614

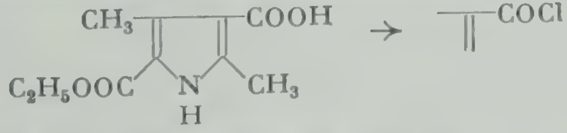
Acetohalogenosugars
s. *7*, 124; s. a. R. G. Hansen, W. J. Rutter, and P. Krichevsky, Biochem. Prep. *4*, 1 (1955)

Acetyl chloride CH_3COCl

Halides from ethers OR → Hal
s. *7*, 582

Carboxylic acid chlorides from carboxylic acids COOH → COCl

4.

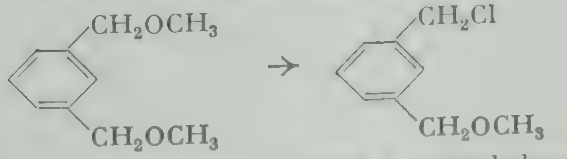


1 g. 5-carbethoxy-2.4-dimethylpyrrole-3-carboxylic acid refluxed 1 hr. with acetyl chloride → 0.98 g. 5-carbethoxy-2,4-dimethylpyrrole-3-carbonyl chloride. S. F. MacDonald, Soc. *1952*, 4176.

Acetyl chloride/zinc chloride $CH_3COCl/ZnCl_2$

Partial replacement of alkoxy groups by halogen OR → Hal

5.



Anhydrous $ZnCl_2$ added to a soln. of 8.5 g. m-xylylene dimethyl ether and acetyl chloride in CCl_4 → 6.7 g. m-methoxymethylbenzyl chloride containing ca. 16% startg. m. F. e. s. F. G. Mann and F. H. C. Stewart, Soc. *1954*, 2819.

Acetyl bromide *CH_3COBr*

Replacement of hydroxyl by bromine OH → Br
s. *9*, 629

Acetobrominolysis of carbohydrates ←
s. *9*, 630

Oxalyl chloride *$(COCl)_2$*

Carboxylic acid chlorides from carboxylic acids COOH → COCl
s. *9*, 474, 877

Formation of sensitive carboxylic acid chlorides
Methyl ketones from carboxylic acids
via carboxylic acid chlorides and acylmalonic acid esters
s. *7*, 583

Oxalyl chloride/potassium salt *$(COCl)_2/K^+$*
s. *9*, 631

α-Bromoisovaleryl bromide *$(CH_3)_2CHCHBrCOBr$*

Bromides from alcohols OH → Br
s. *6*, 581

Silicon tetrachloride *$SiCl_4$*

Carboxylic acid chlorides from carboxylic acids COOH → COCl
s. *7*, 584

Titanium tetrachloride *$TiCl_4$*

Acylchlorosugars OAc → Cl
s. *8*, 614

Stannic chloride *$SnCl_4$*

Cleavage of ethers—Halides from ethers OR → Hal
s. *8*, 615

Phosphorus *P*

Acetobromosugars ←
s. *6*, 582

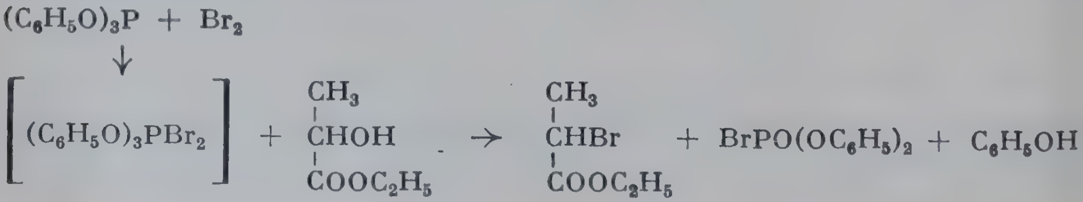
α-Halogenocarboxylic acid halides from carboxylic acids CHCOOH → CHalCOHal
s. *9*, 876, 960

Ethylenebromides from O-heterocyclics

s. *6*, 583

Triphenyl phosphite *$(C_6H_5O)_3P$*

Alkyl halides from alcohols OH → Hal

436.


$$(C_6H_5O)_3P + Br_2 \longrightarrow \left[(C_6H_5O)_3PBr_2\right] + \begin{matrix} CH_3 \\ | \\ CHOH \\ | \\ COOC_2H_5 \end{matrix} \rightarrow \begin{matrix} CH_3 \\ | \\ CHBr \\ | \\ COOC_2H_5 \end{matrix} + BrPO(OC_6H_5)_2 + C_6H_5OH$$

Br added dropwise at 0° to a stirred mixture of ethyl lactate and triphenyl phosphite, allowed to stand at room temp., and the product isolated after a total of 1 hr. → ethyl α-bromopropionate. Y: 82%.—This method is easy, rapid, and it proceeds at low temp. F. e., also with preceding prepn. of triphenyl phoshite dihalide, the method of choice for unsatd. alcohols. s. D. G. Coe, S. R. Landauer, and H. N. Rydon, Soc. *1954*, 2281.

Phosphoric acid/phosphorus pentoxide/potassium iodide $H_3PO_4/P_2O_5/KI$

Iodides from alcohols OH → I

s. *9*, 632

Phosphoric acid/potassium iodide H_3PO_4/KI

Iodides from ethers, alcohols, and ethylene derivatives ←

Tetrahydrofuran ring opening

s. *6*, 584; from alcohols s. a. H. M. Walborsky, M. Baum, and D. F. Loncrini, Am. Soc. *77*, 3637 (1955)

Triphenyl phosphite methiodide $(C_6H_5O)_3PCH_3I$

Alkyl halides from alcohols OH → Hal

s. *8*, 616; s. a. T. H. Bevan, T. Mallein, and D. B. Smith, Soc. *1955*, 1383

Phosphorus trichloride PCl_3

Carboxylic acid chlorides from carboxylic acids COOH → COCl

s. *6*, 585

Phosphorus tribromide PBr_3

Replacement of hydroxyl by halogen OH → Hal

s. *9*, 633

Replacement of sec. and tert. hydroxyl

s. *3*, 466; s. a. R. G. Kelso et al., Am. Soc. *77*, 1751 (1955)

Phosphorus tribromide/quinoline hydrochloride ←

s. Quinoline hydrochloride/phosphorus tribromide

Phosphorus oxychloride $POCl_3$

s. a. under Triethylamine, Dimethylaniline, Calcium carbonate

Replacement of hydroxyl by chlorine, ←

also with simultaneous replacement of alkoxyl

s. *8*, 617

9-Chloroacridines from acridones ←

with protection of an amino group

Urethans from amines

s. *6*, 586

Phosphorus oxychloride/phosphorus pentachloride $POCl_3/PCl_5$

Replacement of hydroxyl by chlorine OH → Cl

s. *7*, 585; partial replacement s. *9*, 634

Phosphorus pentachloride PCl_5

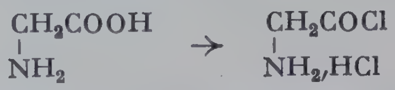
1,1-Dichlorides from ketones CO → CCl_2

s. *6*, 587

1-Chloro-2-trichloroacetylsugars ←
s. *8*, 18

Carboxylic acid chlorides from carboxylic acids COOH → COC
s. *7*, 325; *9*, 650

437.



$$\underset{NH_2}{CH_2COOH} \rightarrow \underset{NH_2,HCl}{CH_2COCl}$$

Aminocarboxylic acid chlorides. PCl_5 added to a suspension of glycine i CCl_4, in which it dissolves, and shaken vigorously in a stoppered vesse at room temp. for 10 hrs. → glycyl chloride hydrochloride. Y: 75-95% F. e. s. S. Levine, Am. Soc. *76*, 1382 (1954).

with simultaneous replacement of hydroxyl by chlorine
s. *6*, 588; α-chlorocarboxylic acid chlorides s. *8*, 934

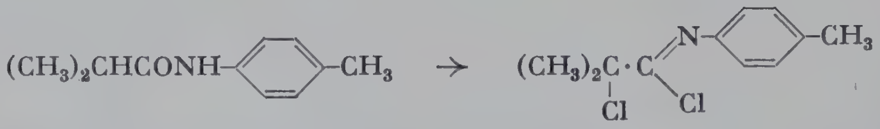
with simultaneous lactam ring closure
s. *9*, 566

Iminochlorides from carboxylic acid amides CONHR → C(:NR)C
s. *6*, 441, 457; *8*, 934, 939

(Carbalkoxyalkylimino)chlorides
from acylaminocarboxylic acid esters
s. *9*, 521

α-Chloroiminochlorides CHCONHR → CClC(:NR)C
from carboxylic acid amides

438.



A mixture of isobutyric p-toluidide and 2 equivalents PCl_5 in dry benzene refluxed 3 hrs. → N-(p-tolyl)-α-chlorisobutyrimino chloride. Y 87%. F. e. s. C. L. Stevens and J. C. French, Am. Soc. *76*, 4398 (1954)

2,6-Dichloropyridines from glutaric acid imides ←
s. *3*, 471; cf. Am. Soc. *76*, 5548 (1954); 2,3,6-trichloropyridines s. L Pichat, C. Baret, and M. Audinot, Bl. *1954*, 88

Phosphinic acid chlorides from phosphinic acids POOH → POC
s. *8*, 618

Thionyl chloride *SOCl*
s. a. under Dimetylaniline, Pyridine, Calcium carbonate

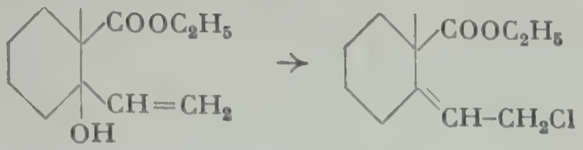
Halides from alcohols OH → Ha

439. $2\ n\text{-}C_4H_9OH + SOCl_2 \rightarrow [(n\text{-}C_4H_9O)_2SO] + SOBr_2 \rightarrow 2\ n\text{-}C_4H_9B$

0.5 mole $SOCl_2$ added dropwise at −10° to a soln. of n-butanol an pyridine in ether, pyridine hydrochloride removed by filtration, th solvent distilled off, pyridine hydrobromide and 0.5 mole $SOBr_2$ added and heated 2 hrs. at 73° → n-butyl bromide. Y: 83%. F. e. s. M. J Frazer et al., Chem. and Ind. *1954*, 931.

s. a. *9*, 108

440.



with simultaneous allyl rearrangement. 1-Vinyl-2-methyl-2-carbethoxycyclohexanol added dropwise with stirring at 0° during 3 hrs. to $SOCl_2$, stirring continued 2 hrs. at 0°, 14 hrs. at 20°, finally 2 hrs. at 80° → β-(2-methyl-2-carbethoxycyclohexyliden)ethyl chloride. Y: 88%. F. e. s. C. A. Grob and J. A. Rumpf, Helv. *37*, 1479 (1954).

Halogenamines from aminoalcohols

s. *7*, 586; chloramines s. *6*, 589

Chlorobromides from bromohydrins Stereochemistry of steroids

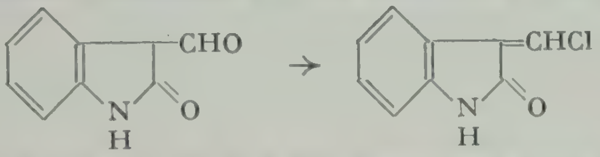
OH → Cl

s. *8*, 619

Halogenomethylene compounds from aldehydes

CH·CHO → C:CHCl

441.



Dry oxindolecarboxaldehyde and $SOCl_2$ warmed slowly with swirling, then refluxed until a clear soln. results → 3-(chloromethylene)oxindole. Y: 94.5%. H. Behringer and H. Weissauer, B. *85*, 743 (1952); s. a. H. Plieninger and C. E. Castro, B. *87*, 1760 (1954).

Carboxylic acid chlorides from carboxylic acids

COOH → COCl

s. *6*, 585; *8*, 104, 134a; *9*, 503; moisture-sensitive compounds s. B. Vassel and W. G. Skelly, Org. Synth. *35*, 28 (1955)

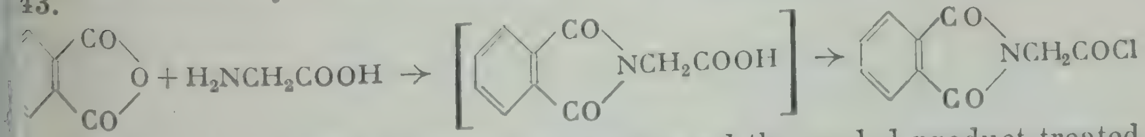
42. **Optically active compounds.** L(+)-Methylethylacetic acid added dropwise during 3 hrs. to pure, ice-salt cooled $SOCl_2$ with frequent agitation, after several hrs. at 0° gradually brought to room temp., whereby the reaction begins slowly and continues at room temp. for 12 hrs., then refluxed 10 min., cooled, and dry air passed through at 0° for 30 min. → L(+)-methylethylacetyl chloride. Y: 76-86%. M. S. Kharasch, J. Kuderna, and W. Nudenberg, J. Org. Chem. *19*, 1283 (1954).

Dicarboxylic acid chloride esters from dicarboxylic acid monoesters

s. *9*, 636

43.

Imidocarboxylic acid chlorides from aminocarboxylic acids



Glycine fused with phthalic anhydride and the cooled product treated with excess $SOCl_2$ → phthaloylglycyl chloride. Y: 90%.—Similarly with succinic anhydride: Succinylgycyl chloride. Y: 60%. A. Neuberger and J. J. Scott, Soc. *1954*, 1820.

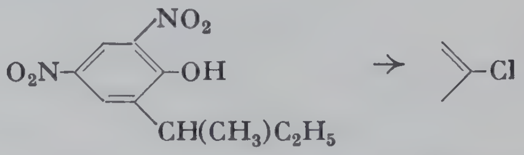
Halogenophthalides from ketocarboxylic acids ○
s. *7*, 855

Halogenocarboxylic acid chlorides from lactones C
s. *7*, 587

Benzenesulfonyl chloride/diethylaniline *$C_6H_5SO_2Cl/C_6H_5N(C_2H_5)_2$*

Chlorides from phenols OH → Cl

444.



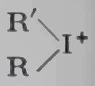
A mixture of DL-2-*s*-butyl-4,6-dinitrophenol, benzenesulfonyl chloride, and N,N-diethylaniline heated 18 hrs. at 100° in a sealed tube → DL-2-*s*-butyl-4,6-dinitrochlorobenzene. Y: 73%.—Other methods were not successful. Also with the optically active compounds s. F. Hawthorne and D. J. Cram, Am. Soc. *74*, 5859 (1952); cf. Synth. Meth. *10*, 120.

Sulfuric acid *H_2SO_4*

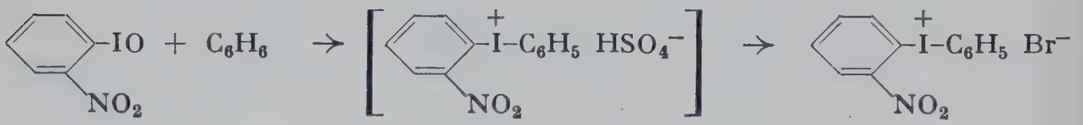
Bromides from alcohols OH → Br
s. *7*, 588

1,2-Dibromides from glycols or glycol monoethers CBrCBr
s. *8*, 916

Unsym. iodonium salts


$R'RI^+$

445.



IO
+ C_6H_6
NO_2
→
$\overset{+}{I}-C_6H_5$ HSO_4^-
NO_2
→
$\overset{+}{I}-C_6H_5$ Br^-
NO_2

o-Nitroiodosobenzene added portionwise during 45 min. at 5° with stirring to a mixture of H_2SO_4 and benzene, the ice bath removed, stirring continued for ca. 3 hrs. until the soln. is negative to starch-iodide paper, poured onto ice, treated with Celite to remove unreacted benzene then with aq. NaBr → 2-nitrodiphenyliodonium bromide. Y: 73-77%.—F. e. in acetic anhydride-glacial acetic acid, and f. methods s. F. M. Beringer et al., Am. Soc. *75*, 2705 (1953).

Dibromides from cyclic ethers C
s. *9*, 597

Sulfuric acid/alkali bromides *$H_2SO_4/NaBr$*

Bromides from alcohols OH → Br

with NaBr s. *8*, 620; with KBr s. S. Berkovic, J. Org. Chem. *20*, 1323 (1955)

Quinoline hydrochloride/phosphorus tribromide

Halides from alcohols via alkoxysilanes ← OH → Hal

446. $(CH_3)_3C{\cdot}CH_2OH + ClSi(C_2H_5)_3 \rightarrow (CH_3)_3C{\cdot}CH_2OSi(C_2H_5)_3 \rightarrow (CH_3)_3C{\cdot}CH_2Br + [BrSi(C_2H_5)_3]$

Triethylchlorosilane added with rapid stirring during 2.5 hrs. to a mixture of neopentyl alcohol (prepn. s. 624), quinoline, and dry benzene, then heated 20 hrs. on a steam bath with stirring → triethylneopentoxysilane (Y: 85%) mixed with PBr_3 and quinoline hydrochloride, then refluxed 16 hrs. → neopentyl bromide (Y: 86%).—This procedure does not give hydrogen halides as reaction products thus avoiding rearrangement of the neopentyl group. L. H. Sommer, H. D. Blankman, and P. C. Miller, Am. Soc. *76*, 803 (1954).

Hydrochloric acid *HCl*

Different reactivity of halides ←
s. *9*, 570

Via intermediates *v.i.*

Replacement of hydroxyl by bromine via sulfonic acid esters OH → Br
s. *7*, 589

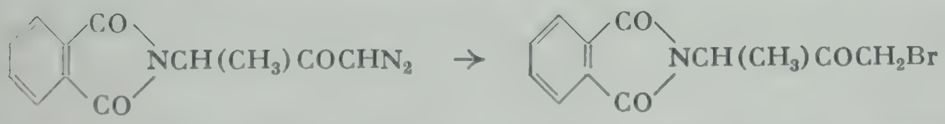
Nitrogen ↑ HalC⇅N

Without additional reagents *w.a.r.*

Replacement of nitro groups by chlorine $NO_2 \rightarrow Cl$
s. *6*, 591

α-Bromoketones from α-diazoketones $COCHN_2 \rightarrow COCH_2Br$

47.



48%-HBr added with stirring to a suspension of (−)-1-diazo-3-phthalimidobutan-2-one in glacial acetic acid, and allowed to stand 1 hr. at room temp. → (−)-1-bromo-3-phthalimidobutan-2-one. Y: 98.5%. F. e. s. K. Balenović, D. Cerar, and L. Filipović, J. Org. Chem. *18*, 868 (1953).

α,α-Dihalogenoketones from α-diazoketones $COCHN_2 \rightarrow COCHHal_2$

48. $C_2Cl_5COCHN_2 \rightarrow C_2Cl_5COCHBr_2$

Diazomethyl pentachloroethyl ketone in CCl_4 stirred and treated during 0.5 hr. with Br in CCl_4, then slowly heated to reflux temp. and refluxing continued for 1 hr. → dibromomethyl pentachloroethyl ketone. Y: 76%.—Also dichloromethyl analog s. A. Roedig and H. Lunk, B. *87*, 971 (1954).

Hydrocarbons and halides from aliphatic azo compounds ←

Free radicals s. *8*, 621

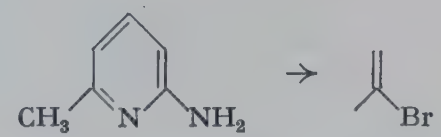
Sodium nitrite *$NaNO_2$*

Replacement of amino groups by halogen $NH_2 \rightarrow Hal$

by fluorine

s. *7*, 590

449.



by bromine. Br added dropwise with stirring at 0° to a soln. of 6-amino-2-methylpyridine in 48%-HBr placed in an ice-salt bath, then aq. $NaNO_2$ added at such a rate that the temp. does not rise above 5°, and stirring continued for 30 min. → 6-bromo-2-methylpyridine. Y: 79%. R. Adams and S. Miyano, Am. Soc. *76*, 3168 (1954); **2-chloropyrimidines** s. I. C. Kogan, R. Minin, and C. G. Overberger, Org. Synth. *35*, 34 (1955).

by iodine

s. *6*, 592

450. $C_3F_7CH_2NH_2 \rightarrow [C_3F_7CHN_2] \rightarrow C_3F_7CH_2I$

via diazo compounds. Aq. Na-nitrite added dropwise with stirring and ice-salt-cooling to a mixture of 1,1-di-H-heptafluorobutylamine, HCl, β,β'-dichlorodiethyl ether, and water, stirring stopped after 1 hr., the separated and dried soln. of 1-H-heptafluorodiazobutane in β,β'-dichlorodiethyl ether cooled with Dry Ice, excess anhydrous HI distilled into it, after 2 hrs. at Dry Ice temp. warmed to room temp. and maintained at that temp. for an additional 3 hrs. → 1,1-di-H-heptafluorobutyl iodide. Y: 58%. L. C. Krogh, T. S. Reid, and H. A. Brown, J. Org. Chem. *19*, 1124 (1954).

Copper *Cu*

Nitration with subsequent replacement of amino groups by halogen ←

s. *6*, 593

Cuprous chloride *CuCl*

Replacement of amino groups by chlorine $NH_2 \rightarrow Cl$

Reverse diazotization

s. *8*, 622

Zinc chloride *$ZnCl_2$*

Chlorides from diazonium chloride-zinc chloride double salts

s. *7*, 591

Fluoboric acid *HBF_4*

Fluorides from amines – Schiemann reaction $NH_2 \rightarrow F$

Heterocyclic fluorides s. 8, 623; decomposition of mixed fluoborates s. J. C. Brunton and H. Suschitzky, Soc. *1955*, 1035

Acetyl chloride *CH_3COCl*

Imidazolidine ring opening C

s. *8*, 624

Halogen ↑ HalC ⇅ Hal

Without additional reagents *w.a.r.*

Replacement of bromine by iodine with simultaneous formation of prim. amines from phthalimides Br → I

s. *8*, 625

Dismutation of dihalides ←

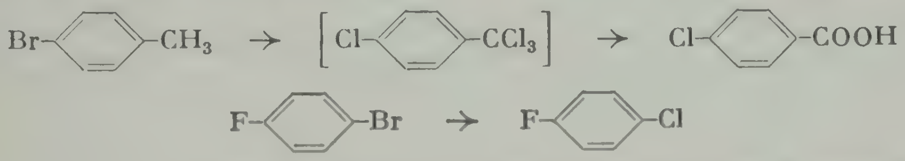
s. *8*, 626

Irradiation ←

Replacement of ar. bromine by ar. chlorine ←

Carboxylic acids from methyl groups via 1,1,1-trichlorides

51.



p-Bromotoluene in CCl_4 irradiated with an UV-lamp and treated with Cl for 5 hrs., the product distilled and stirred 5 hrs. with 85%-H_2SO_4 at 30-50° → p-chlorobenzoic acid. Y: 95%.—p-Fluorobromobenzene chlorinated similarly → p-fluorochlorobenzene. Y: 79%.—Replacement of ar. bromine by chlorine in radical form is a general reaction. F. e. s. W. Voegtli, H. Muhr, and P. Läuger, Helv. *37*, 1627 (1954).

Sodium iodide *NaI*

Iodides from bromides Br → I

s. *7*, 901

Potassium fluoride *KF*

Replacement of bromine and chlorine by fluorine Br (Cl) → F

52. $C_6H_{11}OCOCH_2Br \rightarrow C_6H_{11}OCOCH_2F$

A mixture of cyclohexyl bromoacetate and KF heated 48 hrs. at 195-205° in an oil bath → cyclohexyl fluoroacetate. Y: 74%. E. and O. Gryszkiewicz-Trochimowski and R. Lévy, Bl. *1953*, 462; also replacement of chlorine s. R. Nodzu, H. Kitano, and T. Osaka, J. Chem. Soc. Japan. Ind. Chem. Sect. *58*, 12 (1955); C. A. *49*, 12284b.

Potassium iodide *KI*

Bromides from chlorides Cl → Br

s. *7*, 592

Silver chloride *AgCl*

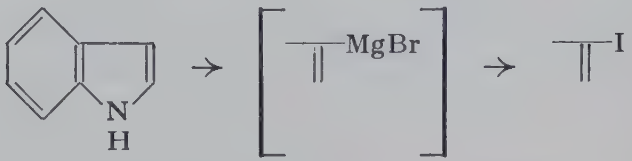
Replacement of bromine by chlorine Br → Cl

s. *8*, 627

Magnesium *Mg*

Replacement of chlorine, bromine, and active hydrogen by iodine ←

453. $C_6H_5Cl \rightarrow C_6H_5I$



Diiodoacetylene (prepn. s. original) in ether added dropwise with ice-cooling to phenyl-MgBr or phenyl-MgCl from bromo- or chloro-benzene and Mg in ether, then allowed to stand 15 min. at room temp. → iodobenzene. Y: 95-97%.

to 3-indole-MgBr from indole and ethyl-MgBr, and the product isolated after 1 hr. → 3-iodoindole. Y: 83%.—Similarly: 1-pentyne → 1-iodopentyne. Y: 91%.

By treating the reaction mixture with dil. H_2SO_4 acetylene is removed as gas, facilitating the isolation of the product. F. e. s. V. Franzen, B. *87*, 1148 (1954).

Aluminum chloride *$AlCl_3$*

Replacement of chlorine by iodine Cl → I

s. *9*, 637

Alkyl iodide *RI*

Formation of quaternary ammonium salts with exchange of halogen ←

s. *8*, 628

Antimony trifluoride/antimony trichloride/chlorine *$SbF_3/SbCl_3/Cl_2$*

Fluorides from chlorides Cl → F

s. *7*, 593

Iodine pentafluoride *IF_5*

Partial replacement of iodine by fluorine I → F

454. $CF_2I \cdot CF_2I \rightarrow CF_3 \cdot CF_2I$

Tetrafluorodiiodoethane added to iodine pentafluoride, the temp. slowly raised until reaction begins at ca. 90°, then more tetrafluorodiiodoethane added dropwise at 90-100° during 5 hrs. → pentafluoroiodoethane. Y: 85%. R. N. Haszeldine and K. Leedham, Soc. *1953*, 1548.

Sulfur ↓

HalC⇅S

Without additional reagents

w.a.r.

Halides from disulfides
s. *9*, 638

RSSR → 2 RHal

Alkylsulfonic acid halides from alkyl halides via alkylthiosulfates
s. *7*, 594

Hal → SO_2Hal

s-Trithiane ring opening
s. *7*, 595

C

Phosphorus pentachloride

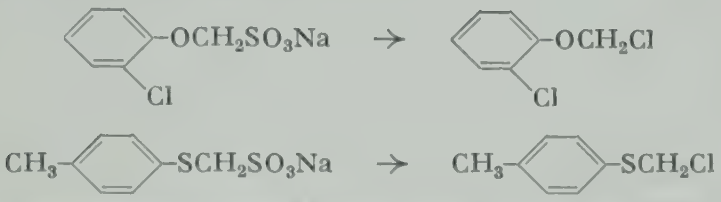
PCl_5

Halides from sulfonates

SO_3^- → Hal

Aryloxy- and arylthio-methyl halides

455.



Na-2-chlorophenoxymethanesulfonate and 2 moles PCl_5 ground together in a mortar, if necessary a little $POCl_3$ added to start the reaction, and the product isolated ca. 15 min. after the first vigorous reaction has subsided → 2-chloro-phenoxymethyl chloride. Y: 90%.—Similarly: 4-Methylphenylthiomethyl chloride. Y: 98%. F. e. and **reactions of aryloxy- and arylthio-methyl halides** s. H. J. Barber et al., J. Appl. Chem. *3*, 266, 259 (1953).

Remaining Elements ↓

HalC⇅Rem

Without additional reagents

w.a.r.

Halides from monoalkylmercury compounds
s. *8*, 594

←

Stannic chloride

$SnCl_4$

Disproportionation – Organotin compounds

←

56. $(n\text{-}C_4H_9)_4Sn + SnCl_4 \rightarrow 2\ (n\text{-}C_4H_9)_2SnCl_2$

Tetra-n-butylstannane cautiously added to anhydrous $SnCl_4$, and heated 3 hrs. at 200-215° with periodic shaking → dichlorodi-n-butylstannane (startg. m. f. 494). Y: 74%. O. H. Johnson and H. E. Fritz, J. Org. Chem. *19*, 74 (1954).

Carbon ↓

HalC⇅C

Without additional reagents

w.a.r.

Acylamines and halides from urethans and carboxylic acid bromides
s. *7*, 597

←

Halogenoketones from ketolactones C
chloroketones s. *7*, 596; bromoketones s. T. Bacchetti and A. Fiecchi, G. *83*, 1037 (1953)

Potassium salt *K+*

α-Halogenocarboxylic acid esters from malonic esters $CH(COOR)_2 \rightarrow CHHalCOOR$
s. *6*, 594

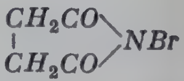
Silver salt *Ag+*

Halides from carboxylic acids COOH → Hal
Hunsdiecker silver salt degradation
s. *9*, 639; chlorides s. R. N. Haszeldine and J. E. Osborne, Soc. *1955*, 3880; modified procedure s. M. Rottenberg, Acta Chem. Scand. *7*, 1001 (1953); W. Parker and R. A. Raphael, Soc. *1955*, 1723

Iodides
Perfluoro compounds as solvents
s. *8*, 629; iodides s. a. R. N. Haszeldine, Soc. *1954*, 4026

Effect of nitro groups
s. *6*, 595

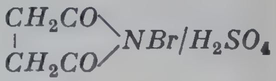
N-Bromosuccinimide



$\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \!\!> NBr$

Replacement of hydrogen and carbon by halogen ←
s. *9*, 640

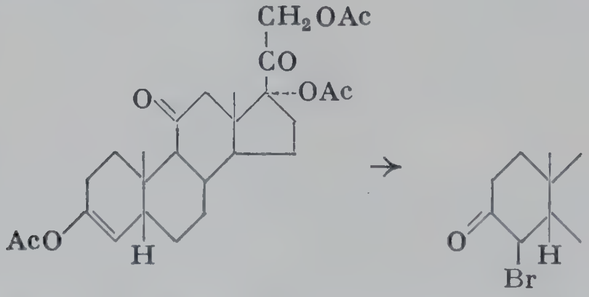
N-Bromosuccinimide/sulfuric acid



$\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \!\!> NBr/H_2SO_4$

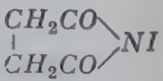
α-Bromoketones from enolesters C:C(OAc) → CBr·CO

457.



A soln. of N-bromosuccinimide in t-butanol followed by 0.8 *N* H_2SO_4 added to a soln. of 3,17α,21-triacetoxy-3-pregnene-11,20-dione in t-butanol, allowed to stand 100 min. at room temp., then treated with aq. Na-sulfite → 17α,21-diacetoxy-4-bromopregnane-3,11,20-trione. Y: 84.1%. R. B. Moffett and H. V. Anderson, Am. Soc. *76*, 747 (1954).

N-Iodosuccinimide



$\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \!\!> NI$

α-Iodoöxo compounds from enolesters C:C(OAc) → CI·CO
s. *9*, 641

α-Acoxyketones from enolesters via α-iodoketones C:C(OAc) → C(OAc)·CO
s. *9*, 642

Sodium hypobromite *NaOBr*
Halides from carboxylic acid amides $CONH_2 \rightarrow Hal$

58. $CF_3CF_2CF_2CONH_2 \rightarrow CF_3CF_2CF_2Br$

Perfluoro compounds. Perfluorocarboxylic acid amides give products different from the amines usually formed by Hofmann degradation.—E: Perfluorobutyramide and water added with ice-cooling to aq. NaOBr prepared from aq. NaOH and Br, stirred 1 hr., the ice bath removed, allowed to warm to 20° during 1 hr., then refluxed 2.5 hrs. → n-perfluoropropyl bromide. Y: 65-70%. F. e. s. D. R. Husted and W. L. Kohlhase, Am. Soc. *76*, 5141 (1954).

Halides from α-ketocarboxylic acid esters COCOOR → Hal
s. *6*, 596

Elimination

Oxygen ↑ HalC ⇑ O

Without additional reagents *w.a.r.*
Cleavage of 1,1-alkoxyhalides to halides ROCHHalR′ → RHal
s. *7*, 598

Nitrogen ↑ HalC ⇑ N

Sodium nitrite *$NaNO_2$*
Halonium salts ←
s. *9*, 643

Sulfur HalC ⇑ S

Without additional reagents *w.a.r.*
Halides from sulfonic acid halides $SO_2Hal \rightarrow Hal$
Thermal decomposition
s. *9*, 644

Formation of S—S Bond

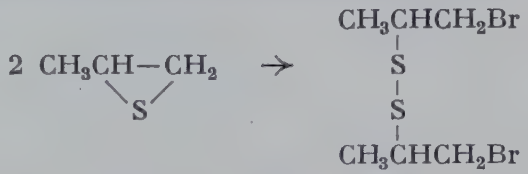
Uptake

Addition to Sulfur and Carbon SS⇓SC

Without additional reagents *w.a.r.*

Sym. 2-halogenodisulfides from ethylenesulfides ←

459.



A soln. of Br in CCl_4 added dropwise with stirring to a chilled soln. of propylene sulfide in the same solvent until a persistent yellow color appears → bis-(1-methyl-2-bromoethyl) disulfide. Y: 88%. Also chloro analog s. J. M. Stewart and H. P. Cordts, Am. Soc. *74*, 5880 (1952).

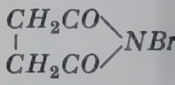
Exchange

Hydrogen ↑ SS⇅H

Sodium nitrite/sodium hydrogen sulfate *$NaNO_2/NaHSO_4$*

Sym. disulfides from mercaptans 2 RSH → RSSR
s. *8*, 630

N-Bromosuccinimide



with simultaneous bromination
s. *8*, 601

Oxygen *O_2*
s. *10*, 461

Sulfur monochloride *S_2Cl_2*

Bisthiuram hexasulfides from dithiocarbamic acids ←
s. *8*, 631

Iodine *I*

Sym. disulfides from mercaptans 2 RSH → RSSR
in the presence of NaOH s. *8*, 632; in the presence of HCl s. H. Böhme, F. Freimuth, and E. Mundlos, B. *87*, 1661 (1954); at pH 7 with I-KI soln. s. E. Walton et al., Am. Soc. *77*, 5144 (1955)

Bisthiuram disulfides from dithiocarbamic acids ←
s. *8*, 633

Hydrochloric acid *HCl*

Disulfonyl trisulfides and thiolsulfonic acid esters from thiosulfonic acids ←
s. *9*, 645

Oxygen ↑

SS⇅O

Without additional reagents *w.a.r.*

Disulfides from sulfenic acid esters and mercaptans ←

s. *8*, 634

Pyridine C_5H_5N

Thiolsulfonic acid esters from sulfonic acid anhydrides RSO_2SR'

s. *9*, 646

Hydrochloric acid *HCl*

Sym. disulfoxides from sulfinic acids $2\ RSO_2H \rightarrow RSO{\cdot}SOR$

s. *6*, 598

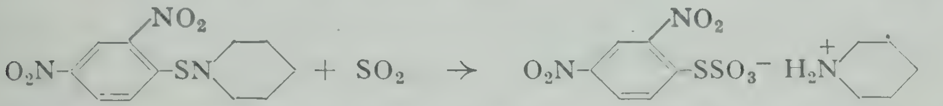
Nitrogen ↑

SS⇅N

Without additional reagents *w.a.r.*

S-Arylthiosulfates from sulfenamides $ArS{\cdot}N\langle \rightarrow ArS{\cdot}SO_3^-$

0.



2,4-Dinitrobenzenesulfenic piperidide dissolved in alcohol with heating, a concd. aq. soln. of SO_2 added, heated almost to boiling, then evaporated under reduced pressure → piperidinium S-2,4-dinitrophenylthiosulfate. Y: almost 100%. F. e., also with unsubst. amides. s. H. Z. Lecher and E. M. Hardy, J. Org. Chem. *20*, 475 (1955).

Halogen ↑

SS⇅Hal

Without additional reagents *w.a.r.*

Disulfides from sulfenylchlorides $RSCl \rightarrow RSSR'$

s. *6*, 599

Potassium hydrogen sulfide *KHS*

Thiosulfonic acid esters from sulfonic acid chlorides via thiosulfonic acids $SO_2Cl \rightarrow SO_2SR$

s. *7*, 599

Lithium aluminum chloride $LiAlH_4$

Sym. disulfides from sulfenylchlorides $2\ RSCl \rightarrow RS{\cdot}SR$

s. *6*, 47

Hydriodic acid *HI*

Sym. disulfides from sulfonic acid chlorides $2\ RSO_2Cl \rightarrow RS{\cdot}SR$

s. *6*, 600

Sulfur ↑

SS⇅S

Without additional reagents *w.a.r.*

Disulfides from thiosulfonic acid esters $RS{\cdot}SO_2R' \rightarrow RS{\cdot}SR''$

s. *7*, 600

Potassium hydroxide

Unsym. from sym. disulfides

s. *8*, 635

KO

RSSR → RSSR

Sodium salt

Reactions with di- and tri-sulfides

s. *6*, 601

Na

←

Remaining Elements ↑

SS⇅Rem

Bromine and sulfur dichloride

Sym. disulfides and trisulfides

s. *7*, 601

Br and SCl

←

Carbon ↑

SS⇅C

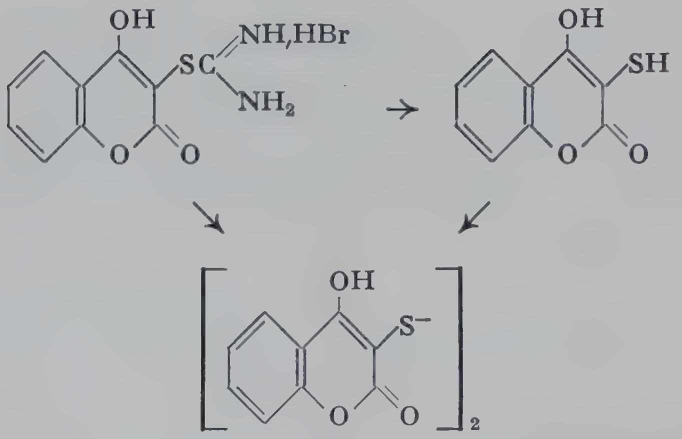
Sodium hydroxide

Mercaptans and sym. disulfides from isothioureas
Sym. disulfides from mercaptans

NaO

←

461.



3-Isothiourea-4-hydroxycoumarin hydrobromide

dissolved in a slight excess of 1%-NaOH soln., and the reaction allowed to proceed at room temp. for 1 hr. →

slowly added to water under N_2, then 5% NaOH soln. added dropwise to yield a clea soln., stirring and N_2-flushing continued fo 0.5 hr. → 3-mercapto-4-hydroxycoumari monohydrate (Y: 81%) dissolved in 1% NaOH soln., and air bubbled through fo 1 hr. →

Y: 83% 3,3′-bis-(4-hydroxycoumarin)disulfide. Y: 87%

H. R. Eisenhauer and K. P. Link, Am. Soc. *76*, 1647 (1954).

Sym. disulfides from thiocyanates

s. *8*, 636

2 RSCN → RSS

Potassium hydroxide/alcohol

s. *8*, 636

KO

Elimination

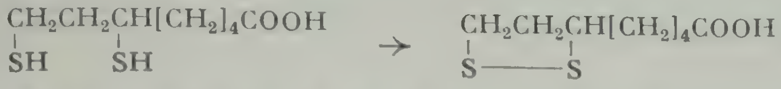
Hydrogen ↑

SS ⇑ H

Ferric chloride/oxygen *FeCl₃/O₂*

Cyclic disulfides from dithiols ○

62.



$$\underset{\text{SH}}{\text{CH}_2}\text{CH}_2\underset{\text{SH}}{\text{CH}}[\text{CH}_2]_4\text{COOH} \rightarrow \underset{\text{S}}{\text{CH}_2}\text{CH}_2\underset{\text{S}}{\text{CH}}[\text{CH}_2]_4\text{COOH}$$

A little $FeCl_3$-soln. added to an aq.-alc. soln. of K-dihydro-6-thioctate prepared from 10.5 g. dihydro-6-thioctic acid and K-carbonate and adjusted to pH 7 with a little HCl, then a rapid stream of oxygen bubbled through the mixture for 20 min. until the color changes to pale yellow → 6.4 g. 6-thioctic acid. F. e. s. M. W. Bullock et al., Am. Soc. *76*, 1828 (1954); s. a. L. J. Reed and C.-J. Niu, Am. Soc. *77*, 416 (1955).

Formation of S—Rem Bond

Uptake

Addition to Sulfur

SRem ⇓ SS

Irradiation ←

Sym. di(alkylthio)mercury from sym. disulfides RSSR → $(RS)_2Hg$

s. *9*, 647

Exchange

Halogen ↑

SRem ⇅ Hal

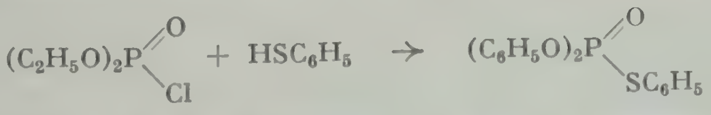
Without additional reagents *w.a.r.*

Selenylsulfides from selenylhalides SeHal → SeSR

s. *6*, 602

Sodium *Na*

Monothiolphosphoric acid esters $(RO)_2P(O)SR'$



$$(C_2H_5O)_2P\genfrac{}{}{0pt}{}{\nearrow O}{\searrow Cl} + HSC_6H_5 \rightarrow (C_6H_5O)_2P\genfrac{}{}{0pt}{}{\nearrow O}{\searrow SC_6H_5}$$

21.5 g. thiophenol added to suspension of Na in benzene, refluxed 3 hrs., cooled, a soln. of 33.7 g. diethyl chlorophosphate in benzene added slowly with stirring, and allowed to stand overnight → 43 g. diethyl S-phenyl thiophosphate. F. e. s. J. Lecocq and A. R. Todd, Soc. *1954*, 2381.

Sodium hydroxide *NaOH*

Thiomercury compounds, organo HgSR

s. *7*, 602

Sodium salt *N*

Organotellurium compounds
s. *9*, 648

Potassium salt

Selenylthiocyanates from selenylhalides SeHal → SeS
s. *6*, 603; *7*, 668

Pyridine C_5H

Alkylthiosilanes from halogenosilanes SiHal → Si
s. *8*, 637

Sulfur ↑ SRem ⇅

Sodium

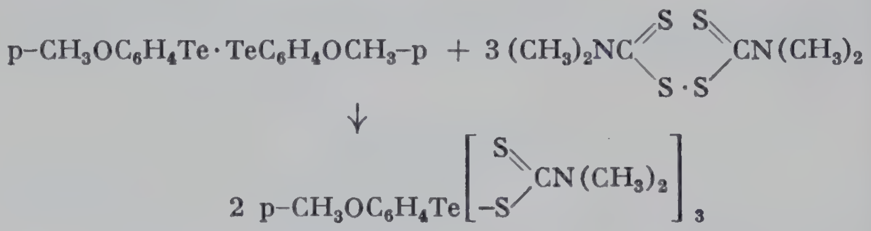
Dithiocarbamyl-selenides and -tellurides from di(thiosulfonyl)-selenides and -tellurides
s. *8*, 638

Remaining Elements ↑ SRem ⇅ Re

Without additional reagents *w.a*

Telluritri(dithiocarbamates) from ditellurides and bisthiuram disulfides

464.



Bis-p-anisyl ditelluride and bis(dimethylthiuram) disulfide in chlo form heated, alcohol added, and heating continued → p-anisyl tellu tri-(N-dimethyldithiocarbamate). Y: ca. 90%. F. e. s. O. Foss, Ac Chem. Scand. *7*, 227 (1953).

Carbon ↑ SRem ⇅

Without additional reagents *w.a*

Cleavage of organobismuth compounds
s. *8*, 639

Formation of S—C Bond

Uptake

Addition to Oxygen and Sulfur SC⇓OS

Magnesium *Mg*

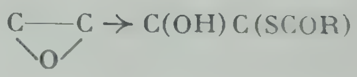
Hydroxysulfones from sultones C
s. *6*, 604

Addition to Oxygen and Carbon SC⇓OC

Without additional reagents *w.a.r.*

Dihydroxyarylthio compounds from quinones ←
s. *8*, 640

Hydroxythiolic acid esters from oxido compounds



s. *9*, 649

Dithiolic acid esters from dicarboxylic acids via dicarboxylic acid anhydrides, carboxythiolic acid esters, and chlorocarbonylthiolic acid esters ←
s. *9*, 650

Hydroxymethylsulfones from sulfinic acids $SO_2H \rightarrow SO_2CH_2OH$
s. *8*, 426

1,1-Hydroxysulfonic acids from aldehydes ←
s. *8*, 641

Oxazoline ring opening C
s. *7*, 603

Sodium *Na*

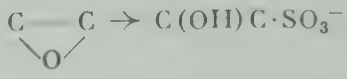
Oxazolone ring opening
s. *6*, 605

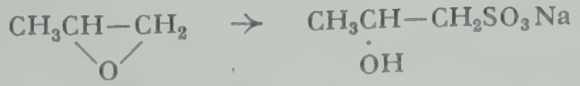
Sodium hydroxide *NaOH*

Hydroxymethylthioethers SCH_2OH
s. *7*, 604

Sodium pyrosulfite *$Na_2S_2O_5$*

2-Hydroxysulfonic acids from oxido compounds





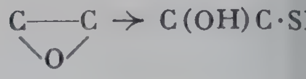
A mixture of Na-metabisulfite and propylene oxide in water stirred 8 hrs. at room temp., then evaporated to dryness → Na-2-hydroxy-1-

propanesulfonate. Y: 85.2%. J. M. Stewart and H. P. Cordts, Am. So
74, 5880 (1952).

Sodium hydrogen sulfite *NaHSC*

1,1-Hydroxysulfonates from aldehydes CHO → CH(OH)SO
s. *10*, 154

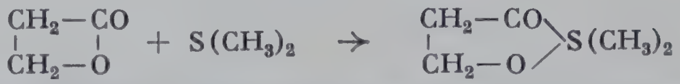
Sodium salt *Na*

Hydroxythioethers from oxido compounds


s. *8*, 642

Hydrochloric acid *HC*

Thetins ←

466.


β-Propiolactone added slowly with stirring to dimethyl sulfide i nitromethane, stoppered, allowed to stand overnight, then a slov stream of dry HCl passed through at 10-25° for ca. 15-20 min. → d methyl-β-propiothetin hydrochloride. Y: 75-78%. N. F. Blau and C. G Stuckwisch, Am. Soc. *73*, 2355 (1954).

Addition to Nitrogen and Carbon SC ⇓ N

Without additional reagents *w.a.*

1,1-Aminothioethers from azomethines N:C → NH·C·S
s. *9*, 651

Amidinothioureas from dicyanodiamides ←
s. *9*, 652; s. a. F. Kurzer, Soc. *1955*, 1; Org. Synth. *35*, 69 (1955)

2,4-Dithiohydantoins from α-aminonitriles C
s. *7*, 606

Aminothioethers from cyclic imines C
s. *8*, 643

Aminomercaptans and thiazolidines from cyclic imines ←
s. *6*, 606

Sodium/alcohol *NaO*

Carboxylic acid thioamides from nitriles CN → CSNH
s. *6*, 608

Ammonia *NH*

s. *6*, 607; s. a. T. S. Gardner, E. Wenis, and J. Lee, J. Org. Chem. 1
753 (1954)

α-Hydroxycarboxylic acid thioamides from cyanohydrins C(OH)CH → C(OH)CSNH
s. *8*, 644

n-Butylamine *n-C_4H_9NH*

Dithioöxaldiimidates from mercaptans ←
s. *9*, 653

Diethylamine $(C_2H_5)_2NH$

Carboxylic acid thioamides from nitriles $CN \rightarrow CSNH_2$
s. *7*, 607

Triethylamine $(C_2H_5)_3N$

Carboxylic acid acylthioethylamides from carboxylic acid ethylenimides ←
s. *9*, 454

Triethylamine/pyridine $(C_2H_5)_3N/C_5H_5N$

Carboxylic acid thioamides from nitriles $CN \rightarrow CSNH_2$
s. *7*, 608

Dithiobiurets $NHCSNHCSNH_2$
s. *7*, 651

Pyridine C_5H_5N

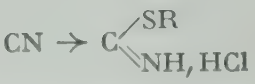
S-Thiocarbamic acid esters from isocyanates and mercaptans $N{:}C{:}O \rightarrow NHCOSR$

67. $C_6H_5NCO + HSCH_2CH_2C_6H_5 \rightarrow C_6H_5NHCOSCH_2CH_2C_6H_5$

A mixture of phenyl isocyanate, β-phenethyl mercaptan and some pyridine allowed to stand 16 hrs. at 25° → N-phenyl-S-(β-phenethyl) thiocarbamate. Y: 97%. D. G. Crosby and C. Niemann, Am. Soc. *76*, 4458 (1954).

Hydrochloric acid *HCl*

Thioimidoester hydrochlorides from nitriles
s. *7*, 609



$CN \rightarrow C\begin{smallmatrix}\diagup SR\\ \diagdown\!\!\diagdown NH, HCl\end{smallmatrix}$

Thioimidoesters and carboxylic acid thioamides from nitriles ←
s. *6*, 608; thioimidoesters s. a. J. B. Jepson, A. Lawson, and V. D. Lawton, Soc. *1955*, 1791

Addition to Halogen and Sulfur SC⇓HalS

Without additional reagents *w.a.r.*

Chlorothioethers from sulfenylchlorides ←
s. *6*, 609

Addition to Sulfur and Carbon SC⇓SC

Without additional reagents *w.a.r.*

4-Mercaptopyrylium salts from 4-thiopyrones ←
s. *8*, 645

Quaternary alkylthioammonium salts ←
s. *8*, 646

Thiazole ring from α-aminonitriles ○
s. *6*, 610; 5-amino-2-hydroxythiazoles s. *6*, 611

Potassium hydroxide/alcohol *KOH*
s. *6*, 610

Addition to Carbon SC ⇓

Without additional reagents *w*

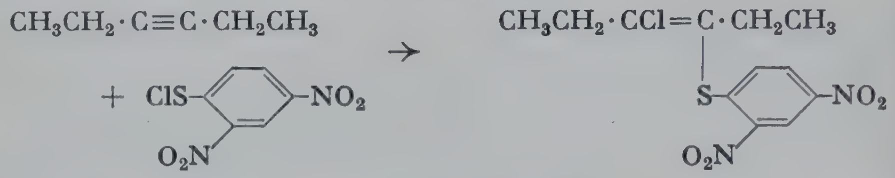
Thioethers from ethylene derivatives C:C → CH
s. *6*, 612

β-Halogenoethyl thioethers from mercaptans $SH \rightarrow SCH_2CH$
s. *8*, 647

Cyanoethyl hydroxyalkyl thioethers from vinyl cyanides C:C → CH
s. *6*, 613

2-Halogenothioenolethers from acetylene derivatives and sulfenylhalides C⋮C → CHal:C

468.



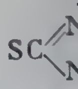
3-Hexyne added to 2,4-dinitrobenzenesulfenyl chloride in a mixture ethylene chloride and glacial acetic acid, allowed to stand 2 hrs. room temp. → 4-chloro-3-(2′,4′-dinitrophenylthio)-3-hexene. Y: 9 —*$AlCl_3$* catalysis is required in the case of acetylene.—The react suggests a practical method for characterizing alkynes. F. e. s. Kharasch and S. J. Assony, Am. Soc. *75*, 1081 (1953).

γ-Ketosulfones from α,β-ethyleneketones C:C → CHCS
s. *4*, 535

Addition of thiolic acids to carbon-carbon double and triple bonds
s. *6*, 614; addition to carbon-carbon double bonds s. E. Walton et Am. Soc. *77*, 5144 (1955)

Acetals from acetylene derivatives via acylthioenols and oximes
Acetyleneacetals – 1,3-Dioxolanes C⋮C → CH:C·SC
s. *7*, 610

Isothiouronium salts
s. *8*, 648



Thiothionophosphoric acid esters $(RO)_2PS$
s. *9*, 654

Cyclic sulfones from dienes
s. *6*, 615

Hexahydro-1,3,6-thiadiazepine-2-thiones and amino-dithiocarbamic acids from imidazolines
Ring enlargement s. *6*, 616

Sodium hydroxide *NaOH*

5-Methyl-2(3H)-thiazolethiones from acetyleneamines via 5-methylene-2-thiazolidinethiones ←

s. *6*, 617

Sodium/alcohol *NaOR*

γ-Ketothioethers from α,β-ethyleneketones C:C → CHCSR

s. *6*, 618

Sodium acetate *CH_3COONa*

Sym. thioethers from ethylene derivatives R_2S

s. *6*, 619

Sodium sulfide *Na_2S*

469. $$Na_2S + 2\ CH_2{=}CHCN \rightarrow S(CH_2CH_2CN)_2$$

Acrylonitrile added dropwise with stirring at 10° to an aq. soln. of Na-sulfide. and stirring continued at room temp. for 4 hrs. → di-(β-cyanoethyl) sulfide. Y: 85%. A. N. Kost and V. G. Yashunskiĭ, Ж. *23*, 230 (1953); C. A. *48*, 2569i.

Triton B ←

S-Cyanoethylation SH → SCH_2CH_2CN

s. *4*, 541; s. a. M. W. Miller, R. W. Amidon, and P. O. Tawney, Am. Soc. *77*, 2845 (1955)

Triton B/piperidine s. Piperidine/triton B

Piperidine *$C_5H_{11}N$*

Thioethers from ethylene derivatives C:C → CHCSR

s. *7*, 611

Mercapturic acids
s. *6*, 620

1,4-Addition
s. *7*, 610

Protection of sulfhydryl groups by addition to ethylene derivatives

Friedel-Crafts ketone synthesis

s. *9*, 655

β-Alkylthio-α-aminocarboxylic acid esters from α-nitro-α,β-ethylenecarboxylic acid esters via β-alkylthio-α-nitrocarboxylic acid esters

s. *6*, 621

Piperidine/Triton B

Thioethers from ethylene derivatives C:C → CHCSR

s. *7*, 611a

Borax/benzoyl peroxide *$Na_2B_4O_7/(C_6H_5COO)_2$*

Sulfonic acids from ethylene derivatives → C:CCHC ·SO_3H

β-H-Perfluoroalkanesulfonic acids

s. *9*, 656

Hydroquinone ←

Cyclic sulfones from dienes ○
s. *6*, 615

Ascaridole ←

Thioethers from ethylene derivatives $C:C \rightarrow CHCSR$
s. *8*, 649

Benzoyl peroxide/borax s. Borax/benzoyl peroxide $(C_6H_5COO)_2/Na_2B_4O_7$

Acetic acid CH_3COOH

γ-Disulfones $C:C \rightarrow CHC\cdot SO_2R$
s. *9*, 657

Sulfur S

Alkylthiotetrahydrothiophenes from dihydrothiophenes $C:C \rightarrow CHCSR$
s. *8*, 650

Thionyl chloride $SOCl_2$

O,S-Acetals from vinyl ethers ←
s. *8*, 651

Dioxane/sulfur trioxide ←

2-Hydroxysulfonic acids from ethylene derivatives $C:C \rightarrow CHC\cdot SO_3^-$
s. *10*, 473

Hydrochloric acid HCl

Ketothioethers from ethylenethioenolethers
Oxo compounds from thioenolethers
Thioethers from ethylene derivatives $C:C \rightarrow CHCSR$
s. *7*, 612

Thioethers – 1,6-Addition SR
s. *6*, 655

α,β-Ethyleneisothiouronium salts from acetylene derivatives ←
s. *8*, 652

β-Mercapto-α-aminocarboxylic acids from ←
α-halogeno-α,β-ethylenecarboxylic acid esters
via inner isothiouronium salts and 4-thiazolinecarboxylic acids
s. *8*, 653

Rearrangement

Nitrogen/Carbon Type SC↶NC

Hydrochloric acid HCl

Aminodithiolcarbonic acid esters ←
from hydroxydithiocarbamic acid esters
s. *9*, 705

Carbon/Carbon Type SC↶CC

Sodium hydroxide $NaOH$

Rearrangement of thiazolidones ←
s. *7*, 613

Exchange

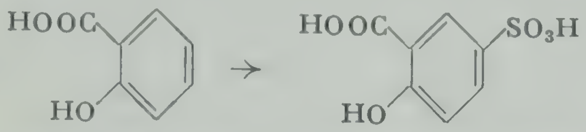
Hydrogen ↑ SC⇅H

Without additional reagents *w.a.r.*

Quinonethioethers – Thioethers from mercaptans ←
Juglones s. *8*, 654

Sulfonation H → SO_3H
s. *7*, 478; *9*, 306; isomers from alkylbenzenes s. F. W. Gray, J. F. Gerecht, and I. J. Krems, J. Org. Chem. *20*, 511 (1955)

470.



Reactions with liq. sulfur trioxide. Sulfan (stabilized liq. SO_3) added dropwise during 13 min. to an agitated suspension of salicylic acid in tetrachloroethylene, whereby the temp. rises to 100°, then gently refluxed for 3 hrs. → 5-sulfosalicylic acid. Y: almost 100%. F. e. s. E. E. Gilbert et al., Ind. Eng. Chem. *45*, 2065 (1953).

Sulfonic acid fluorides from hydrocarbons H → SO_2F
s. *8*, 655

Extended Willgerodt reaction ←
with activated methyl and methylene groups
Carboxylic acid thioamide from methyl groups
Benzothiazole ring synthesis
s. *9*, 658

2(3H)-Benzothiazolethiones ○
s. *8*, 656

1,2-Dithioles from ethylene derivatives
s. *6*, 622; also f. method s. J. Teste and M. Lozać'h, Bl. *1954*, 492

Cupric sulfate/ammonium thiocyanate *$CuSO_4/NH_4SCN$*

1,3(2H)-Benzoxathiol-2-ones
via 2-imino-1,3(2H)-benzoxathioles
s. *7*, 614

Cupric chloride/ammonium thiocyanate *$CuCl_2/NH_4SCN$*

Replacement of hydrogen by thiocyanato groups H → SCN
s. *7*, 615

Aluminum chloride *$AlCl_3$*

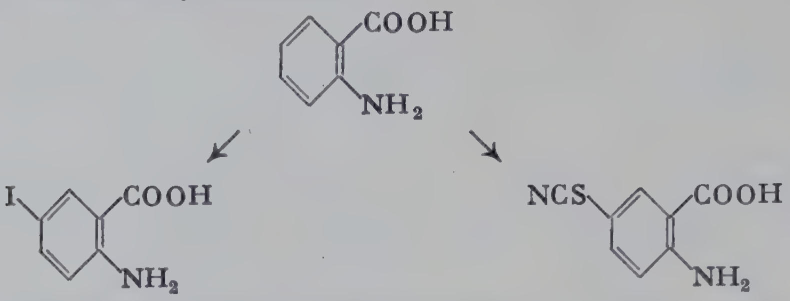
Sym. sulfoxides $2\,RH + SOCl_2 \rightarrow RSOR$
from hydrocarbons and thionyl chloride
s. *7*, 616; s. a. M. Balasubramanian and V. Baliah, Soc. *1955*, 1251

N-Chlorodiethylamine $(C_2H_5)_2NCl$

Replacement of hydrogen by thiocyanato groups and halogen ←

Ar. halogen- and thiocyan-amines

471.



N-Chlorodiethylamine added with ice-cooling to anthranilic acid and
hydriodide | hydrothiocyanate
in 80%-acetic acid, and the product isolated after 0.5-1 hr. →
5-iodo- | 5-thiocyano-
Y: 93%. 2-aminobenzoic acid. Y: 92%.

F. e., also with N-chlorourethan, and brominations, s. A. A. Petrov, G. A. Balaev, and D. V. Ioffe, Ж. *23*, 663 (1953); C. A. *48*, 7584b.

Acetic anhydride $(CH_3CO)_2O$

Sultones from ethylene ketones ○

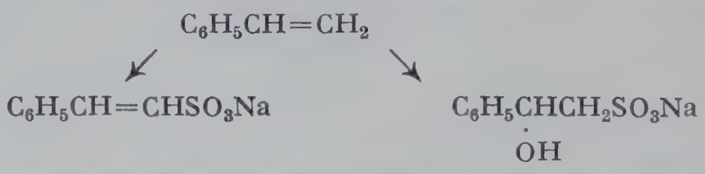
s. *6*, 625

Dioxane/sulfur trioxide

Sulfonation $H \rightarrow SO_3H$

472. **of oxo compounds.** Dioxane-SO_3 is most suitable for sulfonation of aldehydes. For the sulfonation of ketones, SO_3 in dichloroethane, and pyridine-$2SO_3$ my be also used.—E: Dipropyl ketone allowed to react with dioxane-SO_3, and the product isolated as the B-salt → Ba dipropyl ketone sulfonate. Y: 95%. F. e. s. A. P. Terent'ev and L. A. Yanovskaya, Ж. *23*, 618 (1953); C. A. *48*, 6958d.

473.



$$\begin{tikzcd} & C_6H_5CH{=}CH_2 \arrow[dl] \arrow[dr] & \\ C_6H_5CH{=}CHSO_3Na & & \underset{OH}{C_6H_5CHCH_2SO_3Na} \end{tikzcd}$$

Also with simultaneous hydration. A soln. of styrene in ethylene chloride added with stirring to a suspension of dioxane-SO_3 complex in ethylene chloride during 1 hr.

below 10°, the cooling bath removed, stirring continued for an additional hr., allowed to stand overnight, then refluxed 2 hrs. on a steam bath, and isolated as the Na-salt → Na-β-styrenesulfonate. Y: 58-65%.	below 0°, stirring continued for 30 min. at 0°, then hydrolyzed in ice-water without heating, and the product isolated as the Na-salt → Na-2-phenyl-2-hydroxyethane-1-sulfonate. Y: 45-50%.

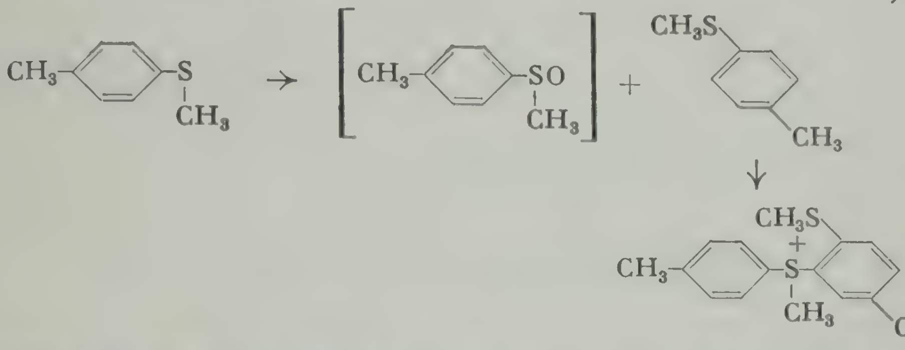
C. S. Rondestvedt, Jr., and F. G. Bordwell, Org. Synth. *34*, 85 (1954).

with migration of a carbon-carbon double bond
s. *6*, 624

Sulfuric acid *H_2SO_4*

Sulfonium salts from 2 thioether molecules via sulfoxides $>S^+$

474.



p-Thiocresol methyl ether added dropwise with stirring during 5 min. to concd. H_2SO_4, and the product isolated after 15 hrs. at room temp., partly as the perchlorate → methyl-p-tolyl-(2-methylthio-5-methylphenyl)sulfonium hydrogen sulfate and perchlorate. Total Y: 98%. F. e., also from the sulfoxides, s. F. Krollpfeiffer and W. Hahn, B. *86*, 1049 (1953).

Bromine *Br*

Replacement of hydrogen by thiocyanato groups H → SCN
s. *7*, 617; *9*, 659

2-Aminothiazole ring ○
s. *6*, 623; *9*, 659

Iodine *I*

2-Aminothiazoles from ketones
s. *7*, 618; s. a. G. N. Mahapatra and M. K. Rout, J. Indian Chem. Soc. *30*, 398 (1953)

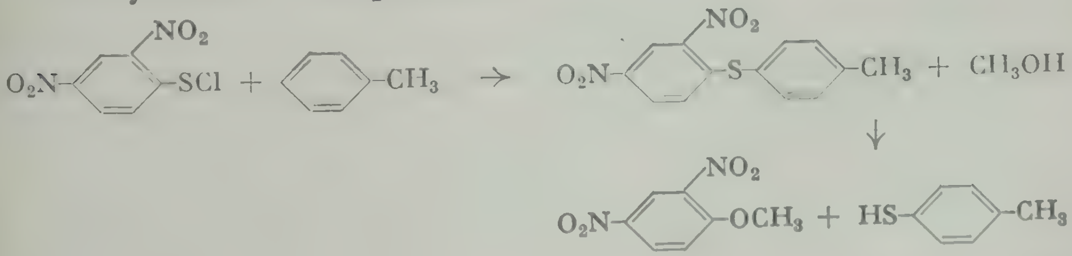
Iodine/thiourea *$I/(NH_2)_2CS$*

Sym. disulfides RSSR
s. *7*, 619

Via intermediates *v.i.*

Replacement of hydrogen by sulfhydryl via thioethers H → SH
Thioethers from sulfenylchlorides
A new synthesis of thiophenols

75.



2,4-Dinitrophenyl p-tolyl sulfide prepared from 2,4-dinitrobenzenesulfenyl chloride and toluene in the presence of $AlCl_3$ at –10° (s. a. Synth. Meth. *7*, 644) added to a soln. of KOH in methanol, and refluxed 30 min. → p-thiocresol (Y: 80%) and dinitroanisole. F. e. s. N. Kharasch and R. Swidler, J. Org. Chem. *19*, 1704 (1954).

Oxygen ↑ SC⇅O

Without additional reagents *w.a.r.*

Cleavage of ethers by mercaptans ←
s. *6*, 626

Alkylthiomethylene from hydroxymethylene and alkoxymethylene compounds C:CHSR
s. *9*, 660

Reactions of hydrogen sulfide and mercaptans at high pressure ←
Reductive formation of polysulfides
s. *9*, 661

Aminomethyl sulfones from sulfonic acid chlorides and sulfinic acids ←

476. $2\ p\text{-}CH_3C_6H_4SO_2Cl$

$$\downarrow$$

$$[2\ p\text{-}CH_3C_6H_4SO_2H] + 2\,H_2CO + H_2NCH_3 \rightarrow (p\text{-}CH_3C_6H_4SO_2CH_2)_2NCH_3$$

p-Toluenesulfonyl chloride added during 15 min. with stirring at 70-80° to an aq. soln. of Na-sulfite and $NaHCO_3$, stirring continued 0.5 hr. at 70-80°, filtered, cooled, a slight excess of 40%-formalin and 30%-methylamine soln. added, finally the product precipitated with concd. formic acid → N-methylbis-(p-toluenesulfonylmethyl)amine. Y: 70.1%.—Mono- and bis-sulfonylmethylamines can also be obtained from sulfinic acids or their salts by an improved one-step procedure (two-step procedure cf. Synth. Meth. *8*, 426). F. e. s. E. Bäder and H. D. Hermann, B. *88*, 41 (1955).

Thiolic acid esters from carboxylic acid anhydrides RCOSR
s. *9*, 686

Thiazolines from glycidic acid esters – Dehydration
s. *6*, 628

Benzothiazolines from aldehydes
s. *8*, 657

4-Thiazolidones from aldehydes
s. *9*, 662

2-Thiazolidinethiones from aminoalcohols
s. *6*, 629

2,4-Diaminothiazoles from α-cyanosulfonates
s. *9*, 663

1,1-Di-(2-benzothiazolyl)alkanes
s. *8*, 659

Thiazolo[5,4-d]pyrimidines
s. *8*, 658

Reaction of hydrogen sulfide with amines in the presence of formaldehyde
Tetrahydro-1,3,5-thiadiazines
s. *9*, 664

Thiazolidines from cyclic imines ←
s. *6*, 606

Sodium hydroxide *NaOH*

Thioethers and ethers from tosylates ←
s. *8*, 660

Thiolic acids from carboxylic acid anhydrides ←
s. *7*, 620

Sodium/alcohol *NaOR*

Thioethers from acoxy compounds OAc → SR
Cleavage of acetals
s. *9*, 665

Sodium acetate *CH_3COONa*

Thiazolidines s. *9*, 666 **Pyrrolo[2,1-b]thiazoles** s. *9*, 667 ○

Sodium thiocyanate *NaSCN*

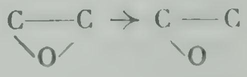
Hydrocarbons from tosylates via thiocyanates OTs → SCN → H
s. *7*, 621

Potassium thiocyanate *KSCN*

Thiocyanates from alcohols OH → SCN
s. *6*, 631

Thiocyanates, sym. thioethers, and sym. disulfides from tosylates ←
s. *8*, 661

Ethylene sulfides from oxido compounds
s. *8*, 662



Sodium sulfide *Na_2S*

Sym. thioethers from tosylates 2 ROTs → R_2S
Anionic displacement reactions of tosylates
s. *8*, 661; a. acoxy compounds, subst. phthalimides, and C-alkylation, with lower yields, among other reactions, s. D. A. Shirley and J. R. Zietz, Jr., J. Org. Chem. *18*, 1591 (1953)

Sym. thioethers from sulfuric acid esters ←
s. *6*, 632

Sodium sulfide/sulfur *Na$_2$S/*

Sym. disulfides from tosylates 2 ROTs → RSS
s. *8*, 661

Sodium hydrogen sulfite *NaHSO*

Sulfonic acids from ethers OR → SO$_3$
s. *7*, 622

Sodium sulfate s. under Zinc chloride, Hydrobromic acid *Na$_2$SO*

Potassium salt *K+*

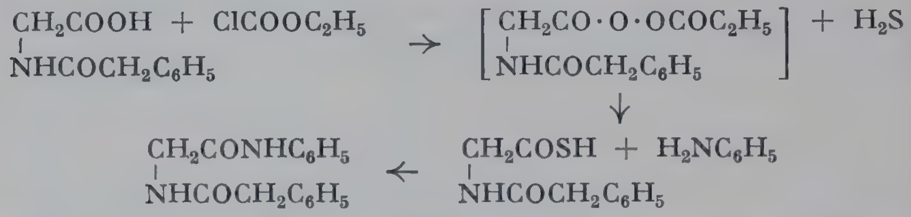
Thioethers from tosylates OTs → S
s. *8*, 663

Thiolic acid esters from tosylates OTs → SCO
s. *6*, 633

Triethylamine *(C$_2$H$_5$)$_3$N*

Carboxylic acid amides and peptides from carboxylic acids via mixed alkoxyformic acid anhydrides and thiolic acids COOH → CON

477.



Phenaceturic acid allowed to react at –10° with ethyl chloroformate and triethylamine in methylene chloride, then treated with excess H$_2$S → thiolphenaceturic acid (Y: 72%) and aniline dissolved in 50:50 ethanol-phosphate buffer pH 7.5, and allowed to stand 18 hrs. at room temp. → phenaceturanilide (Y: 78%). F. thiolic acids and peptides s. J. C. Sheehan and D. A. Johnson, Am. Soc. *74*, 4726 (1952); M. W. Cronyn and J. Jiu, Am. Soc. *74*, 4726 (1952).

Pyridine *C$_5$H$_5$N*

Thiolic acid esters from carboxylic acid anhydrides SH → SCOR
s. *8*, 664

Acylation of 1,1-dithiols C(SH)$_2$ → C(SAc)$_2$
s. *9*, 668

Thiazole ring from o-aminomercaptans via thiazoline ring
s. *6*, 634

Pyridine/phosphorus pentasulfide *C$_5$H$_5$N/P$_2$S$_5$*

Replacement of oxygen by sulfur ←

Carboxylic acid thioamides from carboxylic acid amides
s. *8*, 670

Thiolactams from lactams –NHCO– → –NHCS–
s. *9*, 574

Magnesium *Mg*

Sulfonium salts from sulfoxides ←

s. *8*, 665

Magnesium/ethyl alcohol *Mg/C_2H_5OH*

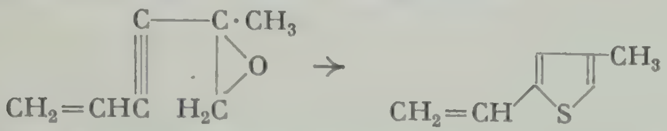
Sulfonylacetic acid esters from sulfonic acid anhydrides via sulfonylmalonic acid esters SO_2CH_2COOR

s. *9*, 669

Barium hydroxide *$Ba(OH)_2$*

Thiophenes from acetyleneoxido compounds

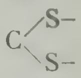
8.



H_2S passed into a well-stirred mixture of $Ba(OH)_2$ in water with simultaneous addition of 2-methyl-1,2-oxido-5-hexen-3-yne at such a rate as to keep the temp. below 50°, followed by the passage of H_2S 1 hr. longer → 2-vinyl-4-methylthiophene. Y: 73-75%.—This is a general method for the prepn. of vinyl- and alkyl-thiophenes. F. e. s. F. Y. Perveev and N. I. Kudryashova, Ж. *23*, 976 (1953); C. A. *48*, 8219i.

Zinc chloride/sodium sulfate *$ZnCl_2/Na_2SO_4$*

Mercaptals



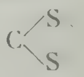
s. *7*, 116; s. a. D. L. MacDonald and H. O. L. Fischer, Am. Soc. *77*, 4348 (1955)

Monothioketals

s. *7*, 605; s. a. Am. Soc. *77*, 568 (1955)

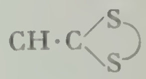
Zinc chloride/hydrochloric acid *$ZnCl_2/HCl$*

Cyclic mercaptals



s. *8*, 666

from α-acoxyketones C(OAc)·CO → CH·



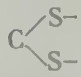
s. *10*, 86

Boron fluoride *BF_3*

Thioethers from mercaptans SH → SR

s. *7*, 623

Mercaptals



s. *8*, 667

Trithioörthocarboxylic acid esters $C(SR)_3$

s. *9*, 670

Aluminum chloride *$AlCl_3$*

Sulfones from sulfonic acid anhydrides RSO_2R'

s. *9*, 671

Ammonium carbonate *$(NH_4)_2CO_3$*

4-Thiazolidones from oxo-compounds

s. *9*, 672

Formic or acetic acid $HCOOH$ or CH_3COOH

Sulfones from sulfinic acids and alcohols RSO_2R'

Alkyl-oxygen fission

s. *9*, 673

Acetic acid CH_3COOH

Thiazolidines ○

s. *6*, 635

Benzothiazolines from aldehydes

s. *8*, 657

Imidazothiazoles

s. *8*, 668

Lead salt Pb^{++}

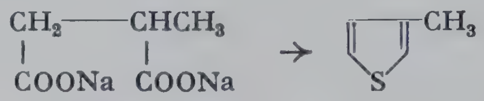
Thiolic acid esters from carboxylic acid anhydrides $RCOSR'$

s. *9*, 674

Phosphorus heptasulfide P_4S_7

Thiophenes ○

479.



A slurry of anhydrous di-Na-methylsuccinate and P_4S_7 in mineral oil added during ca. 1 hr. with vigorous stirring in a slow CO_2-stream at 240-250° to mineral oil at such a rate as to effect fairly rapid distillation, then the temp. raised to 275° and stirring continued for 1 hr. or until distillation ceases → 3-methylthiophene. Y: 52-60%. R. F. Feldkamp and B. F. Tullar, Org. Synth. *34*, 73 (1954).

Phosphorus pentasulfide P_2S_5

Replacement of oxygen by sulfur ←

in N-heterocyclics

s. *6*, 636; s. a. R. K. Robins and G. H. Hitchings, Am. Soc. *77*, 2256 (1955)

1,2-Dithioles

s. *6*, 637

Selective replacement in O-heterocyclics

s. *8*, 669

Thiazoles from α-acylaminocarboxylic acid esters ○

s. *6*, 638

Thiazolo[5,4-d]pyrimidines

s. *6*, 639

Phosphorus pentasulfide/pyridine P_2S_5/C_5H_5N

s. Pyridine/phosphorus pentasulfide

Hydrosulfite $S_2O_4^{--}$

Sulfamic acids from nitro compounds $NO_2 \rightarrow NHSO_3H$

s. *9*, 675

Sodium hydrogen sulfate *$NaHSO_4$*

Thioenolethers from enolethers $C{:}C(OR) \rightarrow C{:}C(SR')$

s. *7*, 624

p-Toluenesulfonic acid *TsOH*

1,1-Disulfones via mercaptals $CO \rightarrow C(SO_2R)_2$

0. $H_2CO + 2\ HSC_6H_5 \rightarrow [H_2C(SC_6H_5)_2] \rightarrow H_2C(SO_2C_6H_5)_2$

A mixture of thiophenol, paraformaldehyde, and p-toluenesulfonic acid heated on a steam bath, after a vigorous exothermic reaction heating continued for 4 hrs., dissolved in glacial acetic acid, 35%-H_2O_2 added dropwise during ca. 1 hr. to the stirred and cooled soln. at such a rate that the temp. is maintained between 45 and 60°, stirring continued for 73 hrs. at room temp. → bis(phenylsulfonyl)methane. Y: 89%. M. W. Cronyn, E. Zavarin, and P. Lim, J. Org. Chem. *19*, 139 (1954).

1,3-Oxathiolane ring ○

s. *9*, 676

4-Thiazolidones from aldehydes

s. *9*, 662

Sulfuric acid *H_2SO_4*

Mercaptans from alcohols $OH \rightarrow SH$

s. *7*, 625

Sulfonium salts from sulfoxides $\rangle S^+$

s. *10*, 474

Hydrochlorides ←

Thiazolidines ○

s. *6*, 640

Pyridine hydrochloride *C_5H_5N,HCl*

Thioenolethers of steroids $C{:}C(SR)$

s. *7*, 626

Hydrofluoric acid *HF*

Thiazolidines ○

s. *6*, 641

Hydrochloric acid *HCl*

Thioethers from acoxy compounds $OAc \rightarrow SR$

s. *6*, 655

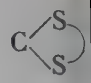
Thioenolethers of steroids $C{:}C(SR)$

s. *6*, 642

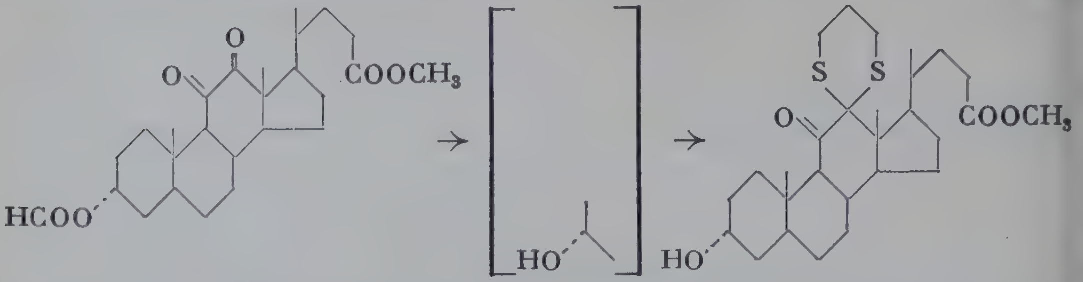
Mercaptals $C\langle^{S-}_{S-}$

s. *6*, 643

Cyclic mercaptals with selective O-deformylation



481.



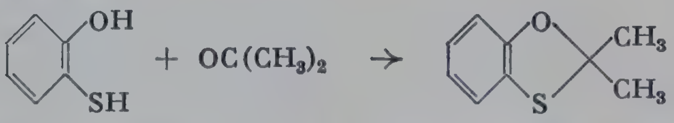
Dry HCl passed through a suspension of methyl 3α-formoxy-11,12-diketocholanate in 9 *N* methanolic HCl with stirring and cooling for 1 hr., after 2 hrs. dry N_2 bubbled through to sweep out methyl formate, resaturated with HCl at 5°, then trimethylenedithiol added in one portion, the HCl-stream maintained for an additional hr., and the reaction mixture let stand for 2 hrs. while the temp. is allowed to rise to 20° → methyl 3α-hydroxy-11,12-diketocholanate-12-trimethylenethioketal. Y: 82%.—When the sweeping with N_2 is omitted, trimethylenedithiol trithioörthoformate is formed as a by-product.—According to H. Hauptmann and M. M. Compos, Am. Soc. *72*, 1405 (1950), trimethylenedithiol gives better yields than the customary ethanedithiol. S. Archer et al., Am. Soc. *76*, 4915 (1954).

Hydrocarbons from ketones via cyclic mercaptals
s. *7*, 627

Mercaptophthalides from o-aldehydocarboxylic acids ○
s. *8*, 671

Benz-1,3-oxathioles

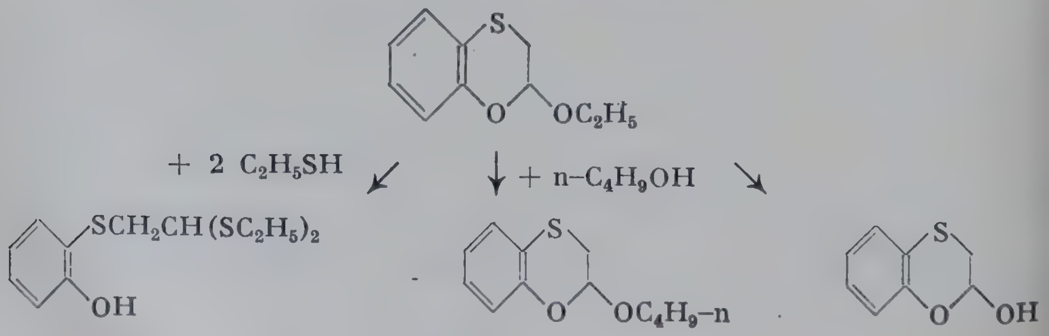
482.



Dry HCl passed into a soln. of 18 g. o-hydroxybenzenethiol in a large excess of acetone for 2 hrs. without control of temp., and then for 30 min. at 0° → 9.6 g. 2,2-dimethylbenz-1,3-oxathiole. F. e. s. D. Greenwood and H. A. Stevenson, Soc. *1953*, 1514.

Benz-1,4-oxathiene ring opening – Transacetalization ←
2-Hydroxy- from 2-alkoxy-benz-1,4-oxathienes

483.



A mixture of 2-ethoxybenz-1,4-oxathiene (prepn. s. 247), ethyl mercaptan, glacial acetic acid, and concd. HCl allowed to stand 6 days at room temp. → diethyl 2-hydroxyphenylthioacetaldehyde mercaptal. Y: 82%. | dry n-butanol, and HCl in ether refluxed 1 hr. → 2-n-butoxybenz-1,4-oxathiene. Y: 79%. | and 3%-H_2SO_4 refl. 34 hrs. → 2-hydroxybenz-1,4-oxathiene. Y: 79.7%.

W. E. Parham and J. D. Jones, Am. Soc. *76*, 1068 (1954).

Stilbenes from aldehydes via s-trithianes ←
s. *9*, 677

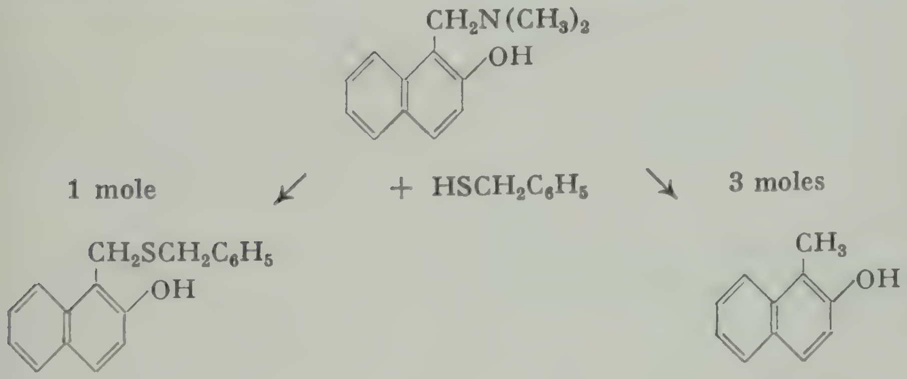
Hydrobromic acid/sodium sulfate *HBr/Na_2SO_4*
Thiolactolides from lactolides OR → SR′
s. *9*, 678

Cobalt polysulfide ←
Mercaptans from oxo compounds or nitriles ←
Thiolactones from ketocarboxylic acids
Sulfactive catalysts
s. *7*, 628

Via intermediates *v.i.*
Thiolic acid esters from carboxylic acids via mixed alkoxyformic acid anhydrides COOH → COSR
s. *8*, 528

Nitrogen ▲ SC⇅N

Without additional reagents *w.a.r.*
Thioethers and hydrocarbons from tert. amines ←



1-Dimethylaminomethyl-2-naphthol and 1 mole benzyl mercaptan heated 1 hr. at 150° in an oil bath → 1-benzylthiomethyl-2-naphthol. Y: 73%. | and 3 moles benzyl mercaptan refluxed 5.5 hrs. → 1-methyl-2-naphthol. Y: 92%.

F. thioethers s. F. Poppelsdorf and S. J. Holt, Soc. *1954*, 1124.

Thioethers from tert. amines – S-β-Acylethylation $NR_2 \rightarrow$
s. *9*, 679; s. a. J. J. Licari and G. Dougherty, Am. Soc. *76*, 4039 (195

Sulfonic acid amides from diazo compounds $>CN_2 \rightarrow >CHSO_2N$
s. *9*, 680

Thioethers from cyclic imines
s. *8*, 672

Potassium hydroxide *KO*

Replacement of amino by alkylthio groups $NH_2 \rightarrow S$
s. *8*, 673

Sodium nitrite *NaN*

Replacement of amino by thiocyanato groups ←
Replacement of nitro by thiocyanato groups
with simultaneous formation of azo compounds by coupling
s. *9*, 681

Sodium sulfite/sulfur dioxide *Na_2SO_3/SO*

Sulfonic acids from quaternary ammonium salts ←
s. *7*, 629

Trimethylamine *$(C_2H_5)_3N$*

Thiazolines from iminoesters
s. *8*, 674

Copper *Cu*

β-Ketothioethers from α-diazoketones $COCHN_2 \rightarrow COCH_2SR$
s. *9*, 682

Sulfinic acids from amines $NH_2 \rightarrow SO_2H$
s. *7*, 630

Thioacetamide *CH_3CSNH_2*

Sym. thioethers from tert. amines $2\,RNR_2' \rightarrow R_2S$
s. *9*, 683

Ammonium chloride *NH_4Cl*

Thioethers from amines ←
s. *9*, 411

Hydrochloric acid *HCl*

Stepwise degradation of peptides
Elimination of terminal moieties
Thiourethans from amines $NH \rightarrow N\cdot CSOR$
s. *7*, 647

Cobalt polysulfide ←

Mercaptans from nitriles $CN \rightarrow CH_2SH$
s. *7*, 628

Via intermediates *v.i.*

Mercaptans from amines $NH_2 \rightarrow SH$
s. *3*, 517; s. a. M. Balasubramanian and V. Baliah, Soc. *1955*, 1251

Halogen ↓ SC ⇅ Hal

Without additional reagents *w.a.r.*

Thioethers from halides Hal → SR
s. *9*, 684

Thioethers from sulfenylbromides SBr → SR
s. *6*, 644

Sym. disulfides from halides 2 RHal → RSSR
s. *9*, 685

Thiolic acid esters from carboxylic acid chlorides COCl → COSR
s. *9*, 650

and carboxylic acid anhydrides
s. *9*, 686

Diacyl sulfides ·COSCO·
s. *7*, 645

1-Alkylthio-1-enamines from carboxylic acid thioamides ←
s. *7*, 631

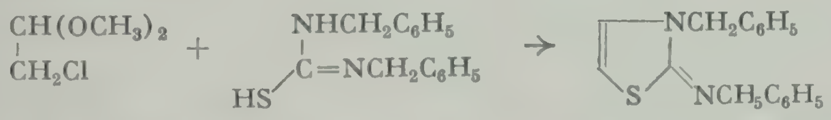
Thiocyanates from mercaptans SH → SCN
s. *9*, 687

Identification of mercaptans as saccharin derivatives ←
s. *9*, 688

S-Alkylation of thiourea derivatives ←
s. *9*, 554

Isothiouronium salts ←
s. *9*, 589

2-Iminothiazolines ○



A mixture of N.N′-dibenzylthiourea, dimethyl chloroacetal, and water heated 16 hrs. on a steam bath → 2-benzylimino-3-benzylthiazoline hydrochloride. Y: 82%. I. A. Kaye and C. L. Parris, Am. Soc. *74*, 2921 (1952).

2,4-Diaminothiazoles from α-halogenonitriles
s. *7*, 632

Hydrazothiazoles
s. *6*, 645

Thiazoles from thiosemicarbazides, also with benzidine rearrangement
s. *6*, 646

2-Mercaptothiazoles from ammonium dithiocarbamate
s. *8*, 675

Benzo-1,4-thiazines
s. *7*, 633

Benzothiazole ring opening
s. *7*, 646

Lithium

Mercaptans from halides
Ethylene derivatives from ethylenesulfides
s. *9*, 689

Sodium

Thioglycosides
s. *7*, 634

Sodium hydride *Na*

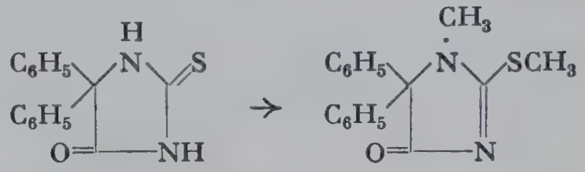
Xanthates and trithiocarbonic acid esters from halides ←
s. *9*, 690

Sodium hydroxide *NaO*

Thioethers from halides Hal → S
s. *8*, 676

Simultaneous S- and N-alkylation

486.



A mixture of 5,5-diphenyl-2-thiohydantoin, methyl iodide, NaOH, metha
nol, and water heated 1.5 hrs. on a steam bath → 1-methyl-2-methy
mercapto-5,5-diphenyl-4(5H)-imidazolone. Y: 72%. C. K. Cain and
K. Naegele, Am. Soc. *76*, 3214 (1954).

Arylthiomethanesulfonates $ArSCH_2SO$
s. *10*, 190

Sodium hydroxide/barium hydroxide *NaOH/Ba(OH*
s. Barium hydroxide/sodium hydroxide

Potassium hydroxide *KO*

Carboxythioethers from halogenonitriles ←
s. *9*, 691

Potassium hydroxide/alcohol

Thioethers from halides Hal → S
s. *10*, 247

Sodium compound ←

Sulfonylthioethers from sulfenylhalides ←
s. *8*, 677

Sodium hydrogen carbonate *$NaHCO_3$*

Thioethers from halides Hal → SR

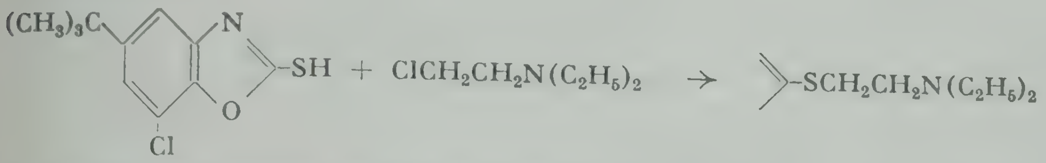
s. *6*, 647

Potassium carbonate *K_2CO_3*

s. *7*, 635; carboxythioethers s. *9*, 692

S-Alkylation

487.



A two-phase mixture of 2-mercapto-5-*tert*-butyl-7-chloro-benoxazole, 2-diethylaminoethyl chloride hydrochloride, K-carbonate, water, and toluene refluxed 14-16 hrs. with stirring → 2-(2′-diethylaminoethylmercapto)-5-*tert*-butyl-7-chlorobenzoxazole hydrochloride (startg. m. f. 207). Y: 95%. F. e. s. L. Katz and M. S. Cohen, J. Org. Chem. *19*, 767 (1954).

Sodium acetate *CH_3COONa*

4-Thiazolidones ○

s. *8*, 678

2-Hydrazino-4-thiazolones from thiosemicarbazones

s. *7*, 636

Potassium thiocyanate *KSCN*

Thiocyanates from halides Hal → SCN

s. *4*, 566; silylmethyl thiocyanates s. J. E. Noll, Am. Soc. *77*, 3149 (1955)

Sodium sulfide *Na_2S*

Benzothiazoles

s. *7*, 637

Sodium disulfide *Na_2S_2*

Mercaptans from halides Hal → SH

Nitromercaptans s. *7*, 638

Sodium hydrogen sulfide *NaHS*

Tert. amines from quaternary ammonium salts with simultaneous replacement of chlorine by sulfur ←

s. *6*, 648

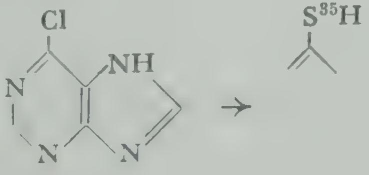
Cyclic thiohydroxamic acids ←

s. *7*, 639

Potassium hydrogen sulfide *KHS*

Mercaptans from chlorides Cl → SH

8.



Labeled compounds. A small amount of a soln. of S^{35}-Ba-sulfide in 0.118 *N* Ba-hydroxide followed by aq. KHS-soln. added to 6-chloropurine, and heated 7 hrs. in a sealed tube in a boiling water bath → S^{35}-6-mercaptopurine. Y: 83%. G. B. Elion and G. H. Hitchings, Am. Soc. *76*, 4027 (1954).

Tert. amines from quaternary ammonium salts with simultaneous replacement of iodine by sulfur ←
s. *8*, 679

Sodium thiosulfate $Na_2S_2O_3$

Alkylthiosulfates from alkyl halides Hal → SSO_3^-
s. *7*, 594

Sodium sulfite Na_2SO_3

Reactions with iodonium salts ←
Sulfonic acids from iodonium salts
s. *9*, 693

Potassium iodide/copper s. Copper/potassium iodide *KI/Cu*

Sodium salt Na^+

Alkylthiomethylsilanes Hal → SR
s. *9*, 694

1,1-Nitrothioethers from sulfenylhalides $C(NO_2)SR$
s. *8*, 680

1,1-Nitrosulfones $C(NO_2)SO_2R$
s. *8*, 681

Thiolic acid esters from carboxylic acid chlorides COCl → COSR
s. *6*, 650

Dithiocarboxylic acid esters CSSR
s. *7*, 640

Xanthates from halides Hal → SCS(OR)
s. *9*, 695

Alkylthiosulfates from halides Hal → SSO_3^-
s. *6*, 651

Bis(triarylthiomethyl) trisulfides ←
s. *9*, 696

Hydroxyethylenesulfones from oxidohalides ←
s. *6*, 649

Potassium salt K^+

Xanthates
- **from alcohols** OH → OCS(SR)
  s. *6*, 841
- **from halides** Hal → SCS(OR)
  s. *6*, 656; *10*, 43

Thiosulfonic acid esters from thiosulfonic acids SO_2SR
s. *7*, 599

Potassium and ammonium salts *K^+ and NH_4^+*

1,3,4-Thiadiazines via α-(dithiocarbazyl)oxo compounds ○

s. *9*, 697

Ammonia *NH_3*

Thioethers from halides Hal → SR

s. *6*, 652

Triethylamine *$(C_2H_5)_3N$*

Ethylenethioethers from ethylenehalides Br → SR

489. $CH_3SH + BrCH_2CH{=}CHCOOCH_3 \rightarrow CH_3SCH_2CH{=}CHCOOCH_3$

Cooled methyl mercaptan added at –10° to methyl γ-bromocrotonate in abs. ether, then triethylamine added dropwise with vigorous stirring during 1 hr., stirring continued 1 hr. at –10° and 4 hrs. at reflux temp. → methyl γ-methylthiocrotonate. Y: 71%.—With Na-methoxide, addition to the double bond also takes place, and other *tert.* amines give lower yields or no reaction. L. Birkofer and I. Hartwig, B. *87*, 1189 (1954); s. a. K. D. Gundermann, A. *588*, 167 (1954).

Thiolurethans from mercaptans SH → SCON<

s. *7*, 641

Pyridine *C_5H_5N*

Hydroxythioethers from hydroxymercaptans SH → SR

s. *9*, 698

Thiolurethans from mercaptans SH → SCON<

Large batches s. *7*, 642

Copper/potassium iodide *Cu/KI*

Thioethers from halides Hal → SR

s. *8*, 909

Barium hydroxide/sodium hydroxide *$Ba(OH)_2/NaOH$*

2-Hydroxythiazoles ○

s. *7*, 643

Calcium carbonate *$CaCO_3$*

Thioethers from halides Hal → SR

s. *9*, 699

Magnesium *Mg*

Mercaptans from halides Hal → SH

from bromides s. *9*, 700; S-labeled compounds from chlorides s. P. T. Adams, Am. Soc. *77*, 5357 (1955), from bromides s. R. C. Thomas and L. J. Reed, Am. Soc. *77*, 5446 (1955)

Alumina *Al_2O_3*

Mercaptans from halides Hal → SH

s. *6*, 653

Aluminum chloride *$AlCl_3$*

Thioethers from sulfenylchlorides RSCl+HR′ → RSR′

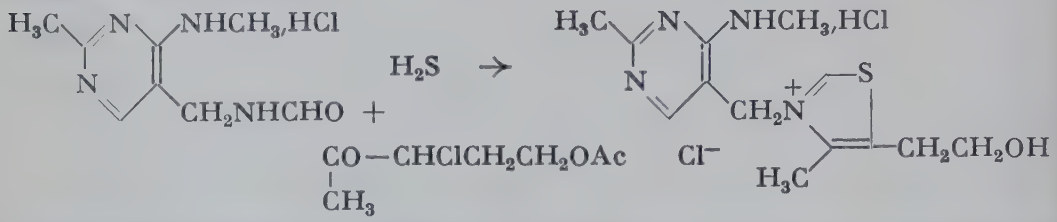
s. *7*, 644; *10*, 475

Ammonium thiocyanate *NH_4SCN*

Thiocyanates from halides Hal → SCN
s. *8*, 682

Formic acid *HCOOH*

Thiazolium chlorides ○

490.


5-Formamidomethyl-2-methyl-4-methylaminopyrimidine hydrochloride added to a mixture of formic acid, activated charcoal, and 3-acetoxy-1-chloropropyl methyl ketone, then H_2S passed through at 115-120° for 5 hrs. → N-methylthiamine chloride hydrochloride. Y: 48%. P. Nesbitt and P. Sykes, Soc. *1954*, 3057.

Thiourea *$SC(NH_2)_2$*

Mercaptans from halides Hal → SH
s. *8*, 516

Phosphorus pentasulfide *P_2S_5*

Thiazole ring from carboxylic acid amides
s. *8*, 683

Hydrobromides

1,3-S,N-Heterocyclics
1,3-Thiazines s. *6*, 654

Hydrochloric acid *HCl*

Thioethers from acoxy compounds and chlorides ←
1,6-Addition s. *6*, 655

Via intermediates *v.i.*

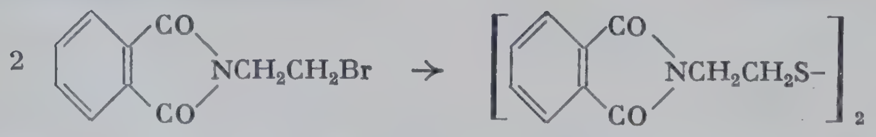
Mercaptans from halides Hal → SH

via isothioureas
s. *1*, 493-5; s. a. M. W. Miller, R. W. Amidon, and P. O. Tawney, Am. Soc. *77*, 2845 (1955)

via xanthates
s. *6*, 656

Carboxymethylthioethers from halides Hal → SCH_2COOH
s. *6*, 657

Sym. disulfides from halides 2 RHal → RSSR

491.


A mixture of bromoethylphthalimide and Na-thiosulfate in methanol-water refluxed 4 hrs., refluxing continued in an extractor with iodine in the thimble over a period of ca. 4 hrs. → di(phthalimidoethyl) disulfide. Y: 83%. M. Viscontini et al., Helv. *37*, 375 (1954).

Sulfur ↑ SC⇅S

Without additional reagents *w.a.r.*

S-Acylation SH → SAc
s. *9*, 701

Sodium hydroxide *NaOH*

S-Alkylation SH → SR
s. *10*, 309

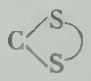
Sodium/liq. ammonia *Na/NH$_3$*

Thioethers from disulfides RSSR → 2 RSR′
s. *6*, 658

with simultaneous N-decarbobenzoxylation
s. *8*, 684

Hydrochloric acid *HCl*

Cyclic mercaptals from alkyldi(thiosulfates)
s. *6*, 659



Nickel *Ni*

Sym. thioethers from mercaptans 2 RSH → RSR
s. *8*, 691

Via intermediates *v.i.*

Thioethers and mercaptans from disulfides ←
o-Mercaptoazo compounds
s. *6*, 660; thioethers from disulfides s. a. Soc. *1954*, 90

Remaining Elements ↑ SC⇅Rem

Without additional reagents *w.a.r.*

Thiocyanates SCN
s. *8*, 685

Sodium/alcohol *NaOR*

Thioethers from thiolthionophosphoric acid esters and alcohols ←
s. *9*, 702

Iodine *I*

Thiazoles from α-ketomercury compounds ○
s. *8*, 686

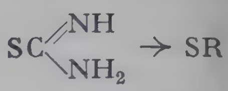
Carbon ↑ SC⇅C

Without additional reagents *w.a.r.*

Transetherification of thioethers SR → SR′
s. *6*, 661

Sodium hydroxide *NaOH*

Thioethers from isothioureas



$$SC\begin{matrix}\diagup NH\\ \diagdown NH_2\end{matrix} \rightarrow SR$$

s. *5*, 456; s. a. J. H. Biel et al., Am. Soc. *77*, 2250 (1955)

Sodium hydrogen carbonate *$NaHCO_3$*

Thioethers from isothioureas and ethylene derivatives C:C → CHCSR

s. *8*, 687

Hydrochloric acid *HCl*

Transmercaptalization ←

Transetherification of thioenolethers

492. $$C_6H_5CH(SC_2H_5)_2 + 2\ HSCH_2C_6H_5 \rightarrow C_6H_5CH(SCH_2C_6H_5)_2$$

A stream of HCl-gas passed through a mixture of benzaldehyde diethylmercaptal and excess benzyl mercaptan for 2 hrs. → benzaldehyde dibenzylmercaptal. Y: 77%.—Also thioenolethers are able to undergo interchange reactions with mercaptans. F. e. and limitations s. M. M. Campos and H. Hauptmann, Am. Soc. *74*, 2962 (1952).

Via intermediates *v.i.*

Benzo-1,4-thiazine from benzothiazole ring ←

Benzothiazole ring opening

s. *7*, 646

Elimination

Hydrogen ↑ SC⇑H

Without additional reagents *w.a.r.*

Thianthrenes from disulfides – Disproportionation ○

s. *6*, 662

Bromine *Br*

Thiazole ring from isothiocyanates via thioureas

s. *8*, 688

Ferric chloride *$FeCl_3$*

1,3,4-Thiadiazoles from thiosemicarbazones

s. *8*, 689

Oxygen ↑ SC⇑O

Sodium hydrogen carbonate *$NaHCO_3$*

Cyclic thioethers by deacylation ○

s. *9*, 703

Acetic anhydride *$(CH_3CO)_2O$*

5-Thiazolones

s. *9*, 704

Phosphoric acid H_3PO_4

1,3,4-Thiadiazoles from acylthiosemicarbazides
s. *6*, 663

Thionyl chloride $SOCl_2$

Thiazolines
s. *9*, 705

via hydroxymethyl compounds
s. *8*, 690

Hydrochloric acid HCl

Thioöxindoles from o-mercaptophenylacetic acids
s. *9*, 121

Thiazolines
s. *6*, 664

Aminodithiolcarboxylic acid esters via hydroxydithiocarbamic acid esters and thiazolines
s. *9*, 705

Nitrogen ↑ SC ⇑ N

Hydrochloric acid HCl

Stepwise degradation of peptides ○
Elimination of terminal moieties

Thiourethans from amines
s. *7*, 647

2-Thiothiazolidones
s. *6*, 665

Halogen ↑ SC ⇑ Hal

Sodium hydrogen carbonate $NaHCO_3$

Ethylenesulfides from halogenomercaptans ○
s. *7*, 648

Aluminum chloride $AlCl_3$

Cyclic sulfones from sulfonic acid chlorides
s. *9*, 706

Sulfur ↑ SC ⇑ S

Sodium cyanide $NaCN$

Bisthiuram sulfides from bisthiuram disulfides ←
s. *7*, 649

Ammonium acetate CH_3COONH_4

Benzothiazoles from thiosulfuric acids ○
s. *7*, 650

Nickel Ni

Sym. thioethers from mercaptans and sym. disulfides ←
s. *8*, 691

Carbon ↑ **SC ⇑**

Sodium hydroxide *NaOI*

Ethylenesulfides from 1,3-oxathiole ring ←
s. 8, 692

1,2-Dihydro-1-keto-2-thianaphthalenes from rhodanines ←
s. 8, 693

Triethylamine/pyridine *$(C_2H_5)_3N/C_5H_5N$*

Thiohydrolysis – Dithiobiurets ←
s. 7, 651

Phosphorus trichloride *PCl_3*

2,5-Thiazolidiones ○
s. 8, 694

Nickel *Ni*

Sym. thioethers from mercaptals and mixed thioethers from thiolic acid esters with hydrogen-free nickel ←
s. 7, 652

Formation of Rem—Rem Bond

Exchange

Halogen ↑ **RemRem ⇅ Hal**

Sodium/potassium *Na,K*

Disilanes from halogenosilanes and by interchange
s. 8, 695

Potassium *K*

Organoplatinum compounds ←

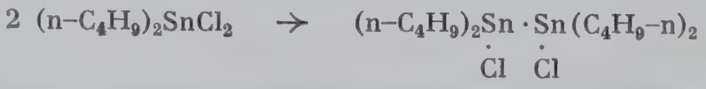
493. $$2\ (CH_3)_3PtI \rightarrow (CH_3)_3Pt\cdot Pt(CH_3)_3$$

2 equivalents of powdered K refluxed 10 hrs. with a soln. of trimethylplatinum iodide in dry benzene, allowed to stand for 2 days, and the last traces of K destroyed with a few drops of n-amyl alcohol → hexamethyldiplatinum. Y: 60%. F. e. s. H. Gilman, M. Lichtenwalter, and R. A. Benkeser, Am. Soc. 75, 2063 (1953).

Sodium/alcohol *NaOR*

Distannanes

494.



$$2\ (n\text{–}C_4H_9)_2SnCl_2 \rightarrow (n\text{–}C_4H_9)_2\underset{Cl}{Sn}\cdot\underset{Cl}{Sn}(C_4H_9\text{–}n)_2$$

A soln. of Na in abs. ethanol added with vigorous stirring during 55 sec. to a soln. of dichlorodi-n-butylstannane (prepn. s. 456) in abs.

ethanol, stirring continued for 1 hr., then allowed to stand overnight → 1,2-dichlorotetra-n-butyldistannane (startg. m. f. 409, 508). Y: 91%. O. H. Johnson and H. E. Fritz, J. Org. Chem. *19*, 74 (1954).

Sodium compound ←

Germanylsilanes ←

s. *7*, 653

Potassium salt K^+

Selenylselenocyanates SeSeCN

s. *7*, 654; improved procedure s. B. *88*, 1 (1955)

Mercury *Hg*

Biarsines

s. *9*, 707

Sulfur ↑ RemRem ⇅ S

Potassium hydroxide *KOH*

Diselenides from selenylsulfides ←

s. *6*, 666

Remaining Elements ↑ RemRem ⇅ Rem

Sodium/potassium *Na,K*

Disilanes by interchange

s. *8*, 695

Carbon ↑ RemRem ⇅ C

Potassium hydroxide and ammonia *KOH and NH_3*

Sym. diselenides from selenocyanates 2 RSeCN → RSeSeR

s. *7*, 655; s. a. H. Reinboldt and E. Giesbrecht, B. *88*, 666 (1955)

Formation of Rem—C Bond

Uptake

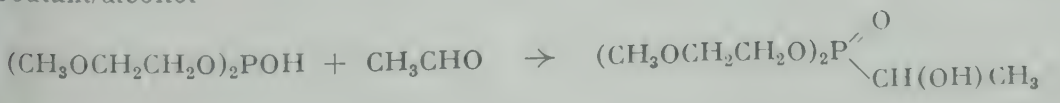
Addition to Oxygen and Carbon RemC ⇓ OC

Without additional reagents *w.a.r.*

α-Hydroxyphosphonic acid esters from oxo compounds CO → C(OH)PO(OR)$_2$

s. *9*, 708

Sodium/alcohol *NaOR*



$$(CH_3OCH_2CH_2O)_2POH + CH_3CHO \rightarrow (CH_3OCH_2CH_2O)_2P(=O)CH(OH)CH_3$$

Di-(2-methoxyethyl) phosphite allowed to react with acetaldehyde the presence of Na-methoxide → di-(2-methoxyethyl) 1-hydrox ethylphosphonate. Y: 79.9%. F. e. s. V. S. Abramov, Y. A. Bochkov and A. D. Polyakova, Ж. *23*, 1013 (1953); C. A. *48*, 8169d.

1-Hydroxy-2-ethylenephosphonic acid esters from α,β-ethylenealdehydes ←
s. *9*, 710

Potassium salt *K*

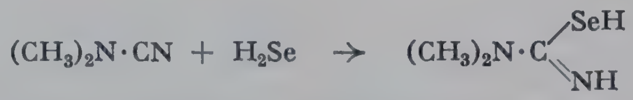
Phosphoric acid esters from oxido compounds ←
s. *6*, 667

Addition to Nitrogen and Carbon RemC ⇓ N

Without additional reagents *w.a.*

Selenoureas NC(:NH)SeH

496.



$(CH_3)_2N\cdot CN + H_2Se \rightarrow (CH_3)_2N\cdot C(SeH){=}NH$

A slow stream of H_2Se passed at room temp. with frequent agitatio through a soln. of dimethylcyanamide in aq. NH_3 for 4-5 hrs. → N,N dimethyselenourea (startg. m. f. 503). Y: 〉75%. F. e., also from carbo diimides, s. R. A. Zingaro, F. C. Bennett, Jr., and G. W. Hammar, J Org. Chem. *18*, 292 (1953).

Addition to Halogen and Carbon RemC ⇓ Hal

Ultrasonic waves ←

in the preparation of organometallic compounds

497. The application of ultrasonic waves may facilitate the preparation o organometallic compounds by providing clean metal surfaces. Grignard reagents, e. g. ethyl-MgBr, can be prepared in moist ether containing other solvents, since ultrasonic waves remove solvent, magnesia or etherate films from the Mg-surface. Al affords organo-Al compounds by reaction of an organo-Mg halide on Al-powder; the use o Al-Mg-alloy is unnecessary. Ultrasonic waves do not overcome, however, the inertia of halogens in the formation of Grignard reagents F. e. s. P. Renaud, Bl. *1950*, 1044.

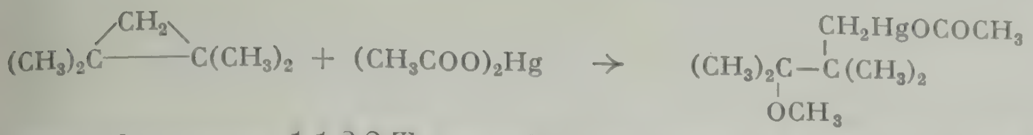
Magnesium/mercuric bromide *Mg/HgBr*

Avoidance of coupling RMgHa
in the preparation of Grignard compounds
Cyclic reactor s. *7*, 656

Addition to Carbon RemC ⇓ C

Without additional reagents *w.a.r.*

Monoalkylmercury compounds ←
s. *8*, 594



from cyclopropanes. 1,1,2.2-Tetramethylcyclopropane and mercuric acetate in abs. methanol kept 3 days at −5° with occasional shaking → 3-methoxy-2,2.3-trimethylbutylmercury acetate (startg. m. f. 509). Y: 71%. F. e., also 3-hydroxy analogs in water, s. R. Y. Levina and V. N. Kostin, ЖК. *23*, 1054 (1953); C. A. *48*, 8171e.

Cyanoethylation of phosphines — PH → PCH_2CH_2CN
s. *9*, 709

β-Ketoselenides from chalcones — C:C → CHCSeR
1,4-Addition s. *7*, 657

Sodium/alcohol — *NaOR*

Reactions with dialkyl phosphites ←
3-Ketophosphonic acid esters from α,β-ethyleneketones
1-Hydroxy-2-ethylenephosphonic acid esters from α,β-ethylenealdehydes
s. *9*, 710

Acyl peroxides — *$(RCOO)_2$*

Silanes from ethylene derivatives — C:C → CHCSi⋛
with acetyl peroxide s. *3*, 534; with benzoyl peroxide s. D. Seyferth and E. G. Rochow, J. Org. Chem. *20*, 250 (1955)

Acetic acid — *CH_3COOH*

Mercurilactones from ethylenecarboxylic acids ←
s. *7*, 658

Rearrangement

Oxygen/Carbon Type — RemC⤸OC

Ethyl iodide — *C_2H_5I*

Phosphonic acid esters from phosphites ←
s. 8, 696

Exchange

Hydrogen ↑ — RemC⇅H

Without additional reagents — *w.a.r.*

Phosphonic acids from hydrocarbons — H → PO_3H_2

$$C_6H_6 \rightarrow [C_6H_5P_4O_{10}H] \rightarrow C_6H_5PO_3H_2$$

Phosphonation. A large excess of benzene heated 24 hrs. with hexagonal phosphoric anhydride (P_4O_{10}) at 275°, and worked up with hot water, whereby the primary reaction product is hydrolyzed → phenylphosphonic acid. Y: 75.5% based on P_4O_{10}. F. e., also isolation as phosphonic dichlorides, s. H. Z. Lecher et al., Am. Soc. *76*, 1045 (1954).

Phosphonyl dichlorides from alcohols OH → $POCl_2$
s. *9*, 711

Phenarsazine ring – Sec. from prim. amines and phenols ○
s. *9*, 713

Lithium *Li*

Organotin compounds $>SnH \rightarrow >SnR$
s. *6*, 668

Sodium *Na*

Phosphinic acids from dichlorophosphines ←
via phosphonous acid monoesters
s. *7*, 659

Sodium amide $NaNH_2$

Organosodium compounds RNa
s. *8*, 697

Sodium hydrogen carbonate $NaHCO_3$

Mercuration $H \rightarrow Hg^+$
s. *6*, 669

Mercuric acetate $(CH_3COO)_2Hg$

Mercurypyrans ○
Organomercuric chlorides from – acetates
s. *9*, 712

Mercuric iodide MgI_2

Acetylenemercury compounds $(RC\vdots C)_2Hg$
s. *8*, 870

Aluminum chloride $AlCl_3$

Phosphorus compounds by Friedel-Crafts synthesis ←
s. *7*, 660

Thiophosphinic acids R_2PSSH

500. $$2\ C_6H_6 + P_4S_{10} \rightarrow (C_6H_5)_2PSSH$$

A mixture of benzene and phosphorus pentasulfide (P_4S_{10}) stirred rapidly at 50° and treated with anhydrous $AlCl_3$ during 3 hrs. at such a rate that the temp. remains at 60-63°, then refluxed 5 hrs. and allowed to stand overnight → diphenylphosphinodithioic acid. Y: 54-80%. Reactions of the phosphinodithioic acid, also conversion into monothiophosphinic acid, s. W. A. Higgins, P. W. Vogel, and W. G. Craig, Am. Soc. *77*, 1864 (1955).

Acetic acid CH_3COOH

Mercuration $H \rightarrow Hg^+$
s. *2*, 576; pyrazole derivatives s. J. L. Finar, Soc. *1955*, 1205

Phosphorus pentachloride *PCl_5*

α,β-Ethylenephosphonic acids from ethylene derivatives H → PO_3H_2

Phosphonation s. *7*, 661

Oxygen *O_2*

Phosphonyl dichlorides from hydrocarbons H → $POCl_2$

Chlorophosphonation

s. *7*, 662

Oxygen ↑ RemC⇅O

Without additional reagents *w.a.r.*

Organotin compounds – Cyanides from hydroxides SnOH → SnCN

s. *9*, 714

Lithium *Li*

Synthesis of silanes from alkoxysilanes ←

s. *9*, 715

Sodium salt *Na^+*

Phosphonic acid esters from phosphites and sulfonic acid esters $PO(OR)_2$

$$n\text{-}C_4H_9OSO_2CH_3 + (C_2H_5O)_2PONa \rightarrow n\text{-}C_4H_9PO(OC_2H_5)_2$$

A soln. of Na diethyl phosphite in tetrahydrofuran added to a stirred soln. of n-butyl methanesulfonate in tetrahydrofuran, and refluxed 6 hrs. → diethyl n-butylphosphonate. Y: 87%.—This reaction provides a convenient route for the conversion of alcohols into phosphonic acids. F. e. s. T. C. Myers, S. Preis, and E. V. Jensen, Am. Soc. *76*, 4172 (1954).

Magnesium *Mg*

Arsonium salts from arsine oxides ←

s. *6*, 670

Iodine *I*

Selenazole ring from selenourea ○

s. *7*, 663

Nitrogen ↑ RemC⇅N

Without additional reagents *w.a.r.*

Organometallic compounds from diazo compounds ←

s. *9*, 716

Sodium nitrite *$NaNO_2$*

Selenocyanates from amines NH_2 → SeCN

s. *7*, 664; s. a. H. Rheinboldt and E. Giesbrecht, B. *88*, 666 (1955)

Cuprous oxide *Cu_2O*

Cyanoarsines from hydrazines via chloroarsines R_2AsC
s. *6*, 671

Cuprous bromide *CuBr*

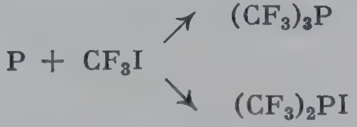
Phosphonic and phosphinic acids from stable diazonium salts ←
s. *9*, 717

Halogen ↑ RemC⇅Hal

Without additional reagents *w.a.r.*

Trifluoromethylphosphorus compounds ←

502.

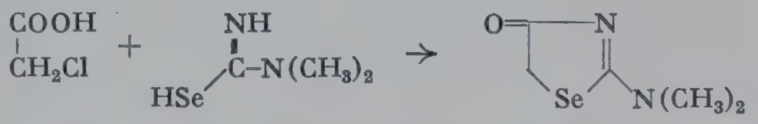


White P heated 48 hrs. with trifluoroiodomethane at 220° in a sealed tube with exclusion of air and moisture → tristrifluoromethylphosphine (Y: 84%) and iodobistrifluoromethylphosphine (Y: 15%). Yields are based on CF_3I consumed, 30% of which is recovered. Also higher yields of iodophosphines and reactions s. F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, Soc. *1953*, 1565.

Tert. arsines R_3As
s. *9*, 718

4-Selenazolones ○

503.



N,N-Dimethylselenourea (prepn. s. 496) added to chloroacetic acid in ethanol, and refluxed 1 hr. → 2-dimethylamino-4-selenazolone hydrochloride. Y: ca. 100%. F. e. s. R. A. Zingaro, F. C. Bennett, Jr., and G. W. Hammar, J. Org. Chem. *18*, 292 (1953).

Lithium *Li*

Silanediols $Si(OH)_2$
s. *8*, 698

Organolead compounds ←
s. *6*, 672; *7*, 665; s. a. J. D'Ans, H. Zimmer, and M. v. Brauchitsch, B. *88*, 1507 (1955)

Organobismuth compounds ←
s. *9*, 719

Sodium *Na*

Tert. arsines R_3As
s. *6*, 673

Potassium hydroxide/alcohol *KOH*

Selenoglycosides ←

s. *7*, 666

n-Butyllithium *n-C_4H_9Li*

Silanes from halogenosilanes SiHal → SiR

Halogen-metal interconversion

s. *9*, 720

n-Butyllithium/magnesium bromide *n-$C_4H_9Li/MgBr_2$*

s. Magnesium bromide/n-butyllithium

Phenyllithium *C_6H_5Li*

Prim. phosphines from halides Hal → PH_2

s. *9*, 721

Triphenylmethylsodium *$(C_6H_5)_3C{\cdot}Na$*

Silico-alkylation of carboxylic acid esters $CH \rightarrow CSi{<}$

s. *9*, 722

Sodium cyanide *NaCN*

Cyano- from chloro-arsines AsCl → AsCN

s. *6*, 671

Potassium thiocyanate *KSCN*

Aryl acetonyl selenides ←

from selenylbromides via selenylthiocyanates

s. *7*, 668

Copper/zinc *Cu,Zn*

Zinc dialkyls R_2Zn

4. $$C_2H_5Br + C_2H_5I \rightarrow (C_2H_5)_2Zn$$

A mixture of ethyl bromide and ethyl iodide added during 2-3 hrs. under N_2 to Cu,Zn-couple from Zn-dust and cupric citrate (prepn. s. original), with cooling when the reaction becomes too vigorous → diethyl zinc. Y: 70%.—This method is especially suitable for small scale laboratory preparations. R. C. Krug and P. J. C. Tang, Am. Soc. *76*, 2262 (1954); cf. C. R. Noller, Org. Synth. Coll. Vol. II, p. 184.

Magnesium *Mg*

Diarylmercury compounds from halides Ar_2Hg

s. *8*, 699

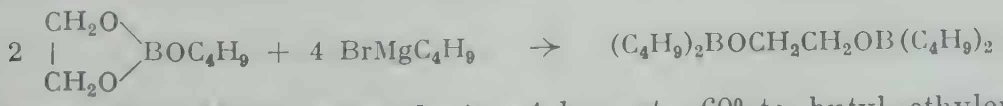
Unsym. organomercury compounds RHgHal → RHgR′

from monoorganomercury compounds

s. *9*, 723

Ethylene dialkyl borinic acid esters ←

from alkyl ethylene boric acid esters



$$2\ \left.\begin{matrix}CH_2O\\ |\\ CH_2O\end{matrix}\right\rangle BOC_4H_9 + 4\ BrMgC_4H_9 \rightarrow (C_4H_9)_2BOCH_2CH_2OB(C_4H_9)_2$$

Ethereal butyl-MgBr added during 4 hrs. at −60° to butyl ethylene borate in ether, hydrolyzed with 3 *N* HCl, ethylene glycol and toluene added to the ether portion, and distilled → ethylene dibutylborinate. Y: 47.4%. F. e. s. R. L. Letsinger and I. Skoog, Am. Soc. *76*, 4174 (1954).

Halogenosilanes from silanols ←
s. *8*, 700

Germanes ←
s. *7*, 669

Organotin compounds ←

506. $4\ CH_3I + SnCl_4 \rightarrow (CH_3)_4Sn$

$SnCl_4$ added dropwise during 2-2.5 hrs. with gentle refluxing to a soln. of methyl-MgI prepared with addition of a few iodine crystals in n-butyl ether, heated 1 hr. at 85-95°, allowed to stand several hrs., then distilled → tetramethyl-Sn. Y: 91%. W. F. Edgell and C. H. Ward, Am. Soc. *76*, 1169 (1954).

Organolead compounds $>PbH \rightarrow >PbR$
s. *6*, 674

Phosphines ←
s. *7*, 670

Phosphine oxides ←

from halides
s. *9*, 724

from phosphinic acids via chlorophosphine oxides
s. *7*, 671

Phosphinic acids R_2POOH

from dialkyl phosphites
s. *8*, 701

Phosphorus(V) from phosphorus(III) compounds
s. *8*, 702

Ar. phosphonic acids, their esters, and triaryl phosphine oxides from chlorophosphoric acid esters ←
s. *8*, 703

Thiophosphonic acids from halides via dithiophosphonic acids ←
s. *7*, 672

Arsines via arsenic magnesium compounds ←
As-Heterocyclics s. *6*, 675

Organobismuth compounds R_3Bi
s. *7*, 673

Magnesium/pyridine *Mg/C_5H_5N*

Phosphinic acids from halides $2\ RHal \rightarrow R_2POOH$
Grignard syntheses of phosphorus compounds
s. *7*, 674

Magnesium/zinc chloride $Mg/ZnCl_2$

Di- and mono-chlorophosphines ←

s. *9*, 725

Phenylmagnesium bromide C_6H_5MgBr

1,4-Azaphosphorines ○

s. *9*, 726

Magnesium bromide/n-butyllithium $MgBr_2/n\text{-}C_4H_9Li$

Organotin compounds ←

Indirect formation of Grignard reagents

s. *7*, 667

Organomercury compounds ←

Synthesis of chlorophosphines from dichlorophosphines PCl → PR

s. *9*, 727

Aluminum chloride $AlCl_3$

Phosphonyl dichlorides from chlorides Cl → $POCl_2$

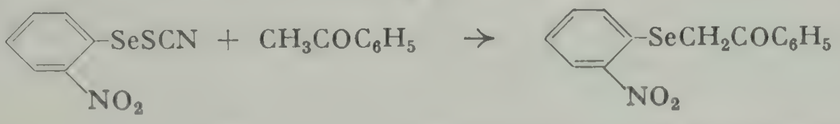
s. *8*, 704

Sulfur ↓ RemC⇅S

Without additional reagents *w.a.r.*

β-Ketoselenides from selenylthiocyanates SeSCN → $SeCH_2COR$

7.



o-Nitrobenzeneselenylthiocyanate dissolved in cold acetophenone, and allowed to stand 24 hrs. at room temp. in a closed flask → o-nitrophenyl phenacyl selenide. Y: 95%. F. e. s. H. Reinboldt and M. Perrier, Bl. *1953*, 379.

s. a. *7*, 668

Remaining Elements ↓ RemC⇅Rem

Lithium *Li*

Organolead compounds ←

s. *8*, 705

Potassium/sodium *K.Na*

Germanecarboxylic acids from digermanes $R_3GeGeR_3 \rightarrow 2\ R_3GeCOOH$

s. *9*, 728

Sodium hydroxide *NaOH*

Unsym. organomercury compounds RHgR′

from monoörganomercury compounds

s. *7*, 675

Sodium iodide *Na*

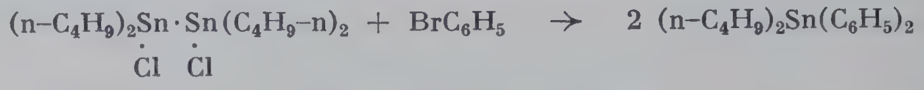
Sym. diorganomercury compounds from monoörganomercury compounds R_2Hg

s. *8*, 706

Magnesium *Mg*

Synthesis of stannanes from halogenodistannanes ←

508.



$$(n\text{-}C_4H_9)_2\underset{Cl}{Sn}\cdot\underset{Cl}{Sn}(C_4H_9\text{-}n)_2 + BrC_6H_5 \rightarrow 2\ (n\text{-}C_4H_9)_2Sn(C_6H_5)_2$$

An ethereal soln. of 1,2-dichlorotetra-n-butyldistannane (prepn. s. 494) added dropwise to ethereal phenyl-MgBr, and stirred an additional 30 min. → diphenyldi-n-butylstannane. Y: 74%. F. e. s. O. H. Johnson and H. E. Fritz, J. Org. Chem. *19*, 74 (1954).

Zinc oxide *ZnO*

Chloroarsines ←

s. *6*, 676

Mercuric chloride *$HgCl_2$*

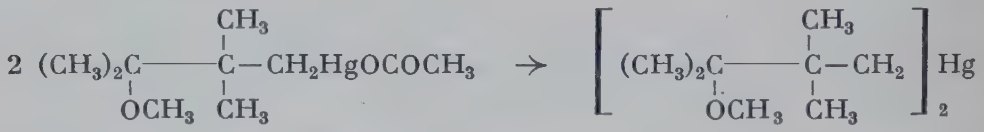
Diarylmercury from aryllithium ←

s. *6*, 677

Stannous chloride/sodium hydroxide *$SnCl_2$/NaOH*

Sym. diorganomercury compounds from monoorganomercury acetates $2\ RHgOAc \rightarrow R_2Hg$

509.



$$2\ (CH_3)_2\underset{OCH_3}{C}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2HgOCOCH_3 \rightarrow \left[(CH_3)_2\underset{OCH_3}{C}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2\right]_2Hg$$

A soln. of $SnCl_2$ in 40%-NaOH added with continuous vigorous stirring to an aq. suspension of 3-methoxy-2,2,3-trimethylbutylmercury acetate (prepn. s. 498), and stirring continued for 1 hr. → bis-(3-methoxy-2,2,3-trimethylbutyl)mercury. Y: 85%. F. e. s. R. Y. Levina and V. N. Kostin, ЖК. *23*, 1054 (1953); C. A. *48*, 8171e.

Bromine *Br*

Selenophene ring from diselenides ○

s. *7*, 676

Carbon ↑ RemC⇅C

Lithium *Li*

Cleavage of silanes and silanols ←

s. *6*, 678

Elimination

Oxygen ↑

RemC ⇑ O

Sulfuric acid *H_2SO_4*

9-Arsafluoreninic acids ○

s. *8*, 707

Hydrobromic acid *HBr*

1,2,3,4-Tetrahydrophosphinolinium salts

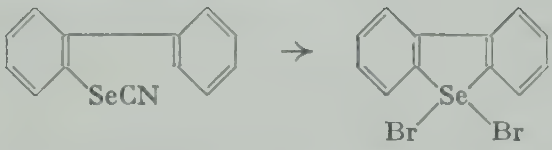
s. *7*, 677

Carbon ↑

RemC ⇑ C

Without additional reagents *w.a.r.*

Selenophene ring from selenocyanates ○



Bromine added dropwise during 3 hrs. with water-cooling to a soln. of 2-selenocyanatodiphenyl in chloroform, cooling continued for another 3 hrs., then allowed to stand 12 hrs. at room temp., finally heated 24 hrs. at 70° → dibenzoselenophene dibromide. Y: 80%. L. Chierici and R. Passerini, Soc. *1954*, 3249.

Via intermediates *v.i.*

1,2,3,4-Tetrahydrophosphinolines
via 1,2,3,4-tetrahydrophosphinolinium salts

s. *7*, 677

Formation of C—C Bond

Uptake

Addition to Hydrogen and Carbon

CC ⇓ HC

Potassium/sodium oxide *K/Na_2O*

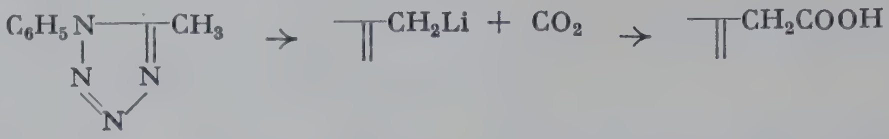
Carboxylation H → COOH

$$C_6H_5CH_3 \rightarrow C_6H_5CH_2Na \rightarrow C_6H_5CH_2COOH$$

Metalation of hydrocarbons. Na-oxide with K-metal makes possible the metalation of toluene in high yield.—E: Toluene allowed to react with K-sand and NaO at 90° for 3 hrs. with vigorous stirring, then the mixture added to Dry Ice → phenylacetic acid. Y: 87%. Ca- or Mg-oxide may also be used. C. E. Claff, Jr., and A. A. Morton, J. Org. Chem. *20*, 440 (1955).

Phenyllithium C_6H_5Li

512.



Metalation of tetrazoles. An ethereal soln. of 1-phenyl-5-methyltetrazole added during 20 min. to ethereal phenyl-Li from bromobenzene and Li, stirred 20 min. under N_2, then rapidly poured over powdered Dry Ice with stirring, and the resulting suspension allowed to stand until all of the Dry Ice has evaporated → 1-phenyl-5-tetrazolylacetic acid. Y: 66%. F. e. s. C. R. Jacobson and E. D. Amstutz, J. Org. Chem. *18*, 1183 (1953).

Triphenylmethylsodium $(C_6H_5)_3C{\cdot}Na$

Introduction of labeled carboxyl-C

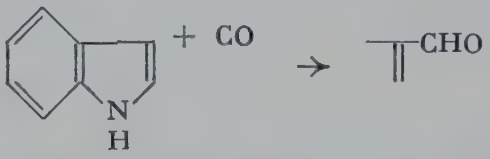
Malonic acid monoesters from carboxylic acid esters

s. *9*, 729

Potassium amide KNH_2

Aldehydes by carbonylation H → CHO

513.



Indole added to KNH_2 prepared from K in liq. NH_3 in the presence of an iron nail, excess NH_3 evaporated, heated ¼ hr. at 170°, allowed to cool to room temp. under N_2, dissolved in dimethylformamide with slight warming, transferred to an autoclave, which is flushed with dry N_2, then filled with CO up to 415 atm./33°, heated to 150°, and shaken 4 hrs. at this temp. → 3-indolecarboxaldehyde. Y: 57%. F. T. Tyson and J. T. Shaw, Am. Soc. *74*, 2273 (1952).

Alkali salts ←

Kolbe synthesis of phenolcarboxylic acids H → COOH

Cation specificity s. *7*, 678

Addition to Oxygen and Carbon CC ⇓ OC

Without additional reagents *w.a.r.*

Synthesis of sec. alcohols from aldehydes CHO → CH(OH)R

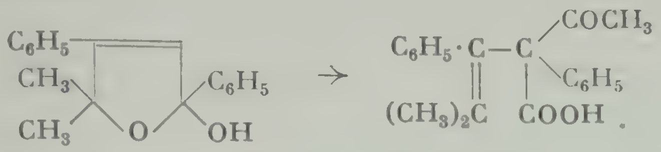
s. *9*, 848

α-Amino-β-hydroxycarboxylic acid esters from aldehydes ←

Cleavage of azomethines

s. *9*, 730

Furan ring opening C



2.4-Diphenyl-5,5-dimethyl-2-hydroxy-2,5-dihydrofuran gently refluxed 40-45 min. with 6 parts acetic anhydride → α-phenyl-α-(1-phenylisocrotyl)-acetoacetic acid. Y: 85-88%. E. D. Venus-Danilova and A. N. Orlova, Ж. *23*, 681 (1953); C. A. *48*, 7597h.

Synthesis of carboxylic acids from lactones
s. *8*, 708

Irradiation ←

Pinacols and sec. alcohols from ketones ←
s. *7*, 679; *9*, 731

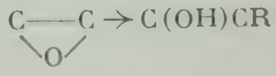
Electrolysis ↯

Pinacols ←
s. *6*, 679; *7*, 680; Hg-plated Cu-gauze cathode s. R. E. Juday and W. J. Sullivan, J. Org. Chem. *20*, 617 (1955)

Benzils from aldehydes via hydrobenzoins ←
s. *9*, 732

Lithium *Li*

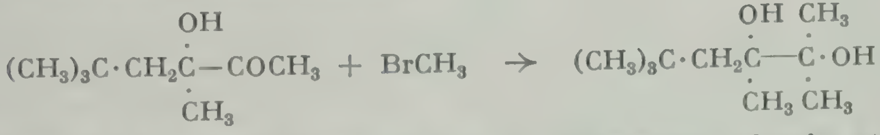
Alcohols from oxido compounds
s. *7*, 681



$$C\text{—}C \rightarrow C(OH)CR$$

Prim. alcohols from cyclic ethers C
s. *8*, 709

Glycols from α-hydroxyketones CO → C(OH)R



$$(CH_3)_3C\cdot CH_2\overset{OH}{\underset{CH_3}{C}}-COCH_3 + BrCH_3 \rightarrow (CH_3)_3C\cdot CH_2\overset{OH}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}\cdot OH$$

3-Hydroxy-3.5,5-trimethylhexan-2-one in ether added slowly at room temp. to methyl-Li from Li and methyl bromide in ether, the bulk of the ether distilled off and the concd. residue refluxed 10 hrs. → 2,3.5,5-tetramethylhexane-2,3-diol. Y: 90%. Also refluxing in benzene after removal of the ether s. W. J. Hickinbottom, A. A. Hyatt, and M. B. Sparke, Soc. *1954*, 2533.

Halogenhydrins from halogenoketones
s. *7*, 682

Syntheses with lithium alkenyls ←
2-Ethylenealcohols from oxo compounds
α.β-Ethyleneketones from carboxylic acids
s. *7*, 683

Sodium amalgam *Na,H*

Pinacols ←
s. *8*, 710

Sodium hydroxide *NaOH*

α-Amino-β-hydroxycarboxylic acids from aldehydes $CHO \rightarrow CH(OH)CH(NH_2)COOH$
s. *6*, 682

Quaternary cyclic enammonium salts via quaternary cyclic β-hydroxyammonium salts ←
s. *8*, 711

Isatogens from o-nitroaldehydes via quaternary cyclic β-hydroxyammonium salts ○
s. *9*, 733

Potassium hydroxide *KOH*

Acetylenealcohols from ketones $CO \rightarrow C(OH)C{:}CR$
in ether s. *3*, 552; diacetylenealcohols in tetrahydrofuran s. W. Chodkiewicz, P. Cadiot, and A. Willemart, C. r. *239*, 885 (1954)

α-Nitroalcohols from aldehydes $CHO \rightarrow CH(OH)CH(NO_2)R$
s. *6*, 772

Potassium hydroxide/acetal *KOH/RCH(OR′)₂*

Acetylenealcohols from oxo compounds $CO \rightarrow C(OH)R$
Syntheses with potassium hydroxide in solvents of the acetal type
s. *9*, 734

Sodium/alcohol *NaOR*

α-Nitroalcohols

from aldehydes $CHO \rightarrow CH(OH)CH(NO_2)R$
s. *8*, 712

from ketones $CO \rightarrow C(OH)CH(NO_2)R$
s. *7*, 685

Lactones from oxido compounds ←
s. *7*, 684

n-Butyllithium $n\text{-}C_4H_9Li$

Halogen-metal interconversion method
Tert. alcohols from ketones $CO \rightarrow C(OH)R$
s. *6*, 680; optimum temp. of the interconversion s. R. L. Morgan et al., Am. Soc. *77*, 5658 (1955)

3-Pyridyl compounds
s. *8*, 713

Phenyllithium C_6H_5Li

C-Hydroxymethylation $H \rightarrow CH_2OH$
s. *8*, 849

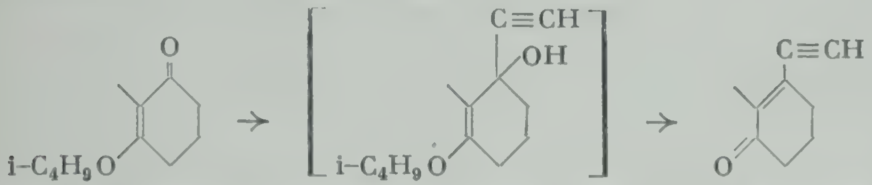
Alcohols from oxo compounds $CO \rightarrow C(OH)R$
s. *9*, 735

Amino-tert-alcohols from aminocarboxylic acid esters $COOR \rightarrow C(OH)R_2$
s. *6*, 681

Lithium/liq. ammonia *Li/NH$_3$*

Ethynylalcohols from oxo compounds $CO \rightarrow C(OH)C{:}CH$
s. *6*, 683; also with dehydrohalogenation (cf. *9*, 736) s. W. M. McLamore, S. Y. P'An, and A. Bavley, J. Org. Chem. *20*, 109 (1955)

3-Acetylene-2-cyclohexenones from 1-alkoxy-1-cyclohexen-3-ones ←



A mixture of 2-methyl-3-isobutoxy-2-cyclohexen-1-one and abs. ether added dropwise with vigorous stirring at 0-10° to an ethereal suspension of Li-acetylenide prepared during 30 hrs. from Li and acetylene in liq. NH_3 with subsequent replacement of the NH_3 by ether, allowed to stand overnight, refluxed 3 hrs., ice-salt cooled, treated with water, then vigorously agitated and treated at 5-15° with concd. H_2SO_4-water 1:2, the product isolated after an additional hr. → 2-methyl-3-ethynyl-2-cyclohexen-1-one. Y: 75-80%. A. Eschenmoser, J. Schreiber, and S. A. Julia, Helv. *36*, 482 (1953).

Lithium amide *LiNH$_2$*

Acetylenealcohols from oxo compounds and α,β-ethylenebromides $CO \rightarrow C(OH)C{:}CH$
s. *9*, 736

Prim. acetylenealcohols from oxido compounds $CH \rightarrow C{\cdot}CH_2CH_2OH$
s. *9*, 737

β-Hydroxycarboxylic acid esters from oxo compounds $CO \rightarrow C(OH)CH_2COOR$
s. *8*, 714; from ketones s. *7*, 686; Am. Soc. *77*, 1050 (1955)

Lithium diethylamide *LiN(C$_2$H$_5$)$_2$*

β-Hydroxycarboxylic acid amides from oxo compounds $CO \rightarrow C(OH)CH_2CONR_2$
s. *8*, 715

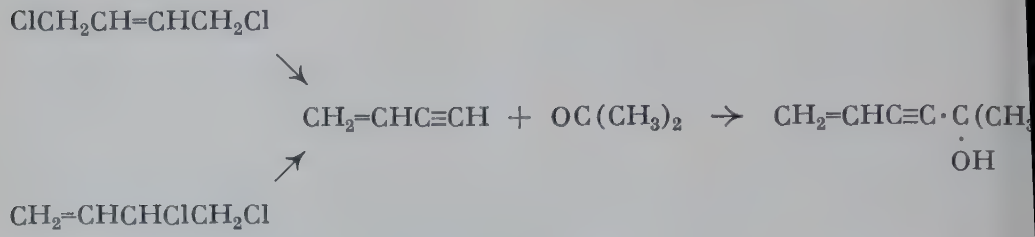
Sodium amide *NaNH$_2$*

Sym. polyacetylene derivatives ←
Syntheses with 1,4-dichloro-2-butyne
s. *7*, 687; syntheses with 1,4-dichloro-2-butyne s. a. J. Colonge and G. Poilane, C. r. *238*, 117 (1954); Bl. *1955*, 499

Tert. alcohols from ketones CO → C(OH

s. *9*, 738

517.



Vinylethinyl compounds. 1,4-Dichloro-2-butene or 1,2-dichloro-3-buten or a mixture of both added at –35° (all te following operations at th same temp.) during 30 min. to a stirred soln. of $NaNH_2$ in liq. NH stirring continued for 3 hrs., anhydrous acetone added during 15 min and again stirred for 3 hrs. → 2-methylhex-5-en-3-yn-2-ol. Y: 56%. e. s. W. J. Croxall and J. O. Van Hook, Am. Soc. *76*, 1700 (1954).

Potassium/liq. ammonia *K/NH*

Acetylenealcohols from ketones CO → C(OH)C:C

Ketones from enolethers

Labeled compounds s. *8*, 716

Sodium hydrogen carbonate *NaHCO*

Hydroxymethylation of ketones $H \rightarrow CH_2O$

s. *6*, 749

Potassium carbonate *K_2CO*

Benzofurans

s. *7*, 688

Diene synthesis with lactones ←

s. *9*, 739

Sodium cyanide *NaC*

α-Hydroxycarboxylic acids from aldehydes via cyanohydrins CHO → CH(OH)COO

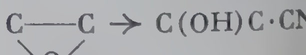
s. *6*, 684

α-Cyanosulfonates from aldehydes $CHO \rightarrow CH(CN)OSO_2$

s. *9*, 663

Sodium potassium cyanide *(Na,K)C*

Halogenocyanohydrins from oxidohalides



$\underset{O}{C\text{—}C} \rightarrow C(OH)C\cdot C$

s. *7*, 689

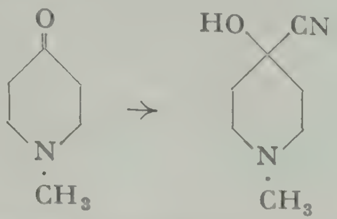
Potassium cyanide *KC*

Enediols from aldehydes 2 CHO → C(OH):C(OH

s. *7*, 690

Cyanohydrins from ketones

CO → C(OH)CN

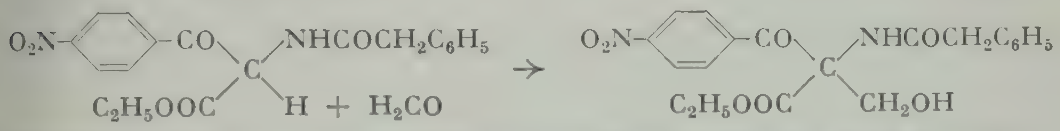


1-Methyl-4-piperidone added to cold satd. aq. KCN-soln., stirred ca. 1 min., then dil. HCl added with external cooling until te soln. is slightly acidic, neutralized with K-carbonate and excess added to salt out the product → 4-hydroxy-1-methylisonipecotonitrile. Y: 87%. Also from the hydrochloride s. R. E. and G. G. Lyle, Am. Soc. *76*, 3536 (1954).

Subst. homophthalic acids from phthalides ←
via o-carboxyphenylacetonitriles and pyrrolo(2′,3′:3,4)isocoumarins
s. *9*, 740; o-carboxyphenylacetonitrile s. a. *3*, 558; improved procedure s. H. Gault and M.Dorgans, Bl. *1954*, 827

Disodium hydrogen phosphate *Na_2HPO_4*

C-Hydroxymethylation H → CH_2OH



30%-formaldehyde soln. containing *sec*-Na-phosphate added to a soln. of 15 g. ethyl p-nitrobenzoylphenacetylaminoacetate in methanol, and allowed to stand 1 hr. → 14.2 g. α-(p-nitrobenzoyl)-N-phenacetylserine ethyl ester. F. e. s. G. Ehrhart, B. *86*, 884 (1953).

Sodium hydrogen sulfite *$NaHSO_3$*

Cyanohydrins from oxo compounds CO → C(OH)CN
from aldehydes s. *4*, 625; from ketones s. H. J. Glenn et al., Am. Soc. *77*, 3080 (1955); A. G. Anderson, Jr., and D. O. Barlow, Am. Soc. *77*, 6048 (1955)

Triethylamine *$(C_2H_5)_3N$*

α,β-Ethylenenitriles from aldehydes via cyanohydrin acetates ←
s. *8*, 717

Piperidine *$C_5H_{11}N$*

5-(α-Hydroxybenzyl)hydantoins ←
s. *8*, 718

Pyridine *C_5H_5N*

C-Hydroxymethylation H → CH_2OH
s. *8*, 690

Cyanohydrins from oxo compounds CO → C(OH)CN
s. *7*, 691

Calcium carbide/potassium hydroxide *CaC_2/KO*

Acetylenediols from ketones ←
s. *8*, 719

Calcium/liq. ammonia *Ca/NH*

Ethynylalcohols from aldehydes CHO → CH(OH)C⋮C
s. *6*, 683

Calcium oxide *CaO*

Hydroxymethylation with simultaneous Cannizzaro reaction ←
s. *7*, 698

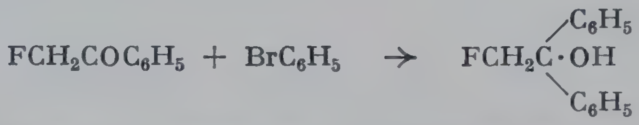
Magnesium *Mg*

Sec. alcohols from aldehydes CHO → CH(OH)R
s. *6*, 685; *7*, 692; α,β-ethylenealcohols s. *6*, 764

Sym. sec. alcohols from halides 2 RHal → RCH(OH)R
s. *7*, 693

Tert. alcohols from ketones CO → C(OH)R

520.



$$FCH_2COC_6H_5 + BrC_6H_5 \rightarrow FCH_2\overset{C_6H_5}{\underset{C_6H_5}{C}}\cdot OH$$

ω-Fluoroacetophenone (prepn. s. 627) can be converted into 1,1-diphenyl-2-fluoroethanol (Y: 65%) if the Grignard reaction with phenylMgBr is carried out rapidly (during 15 min.) at low temp. (0°). Under more drastic conditions intramolecular rearrangement converts the carbinol into desoxybenzoin. F. Bergmann and A. Kalmus, Am. Soc. *76*, 4137 (1954).

s. a. *8*, 911; *9*, 981; O-heterocyclics s. *7*, 694

Effect of the solvent basicity in Grignard reactions

521. A strongly basic solvent (pyridine) retards the reaction between a Grignard reagent and a ketone, while a weakly basic solvent (anisole, phenetole) permits a rapid reaction. A solvent of intermediate basicity (tetrahydrofuran) results in abnormal products. Yields of normal products were uniformly higher in anisole than in ether. E., also with sterically hindered compounds, s. R. N. Lewis and J. R. Wright, Am. Soc. *74*, 1253 (1952).

Acetylenealcohols from oxo compounds CO → C(OH)C⋮CR
s. *6*, 686

Asym. synthesis by Grignard reaction ←
s. *9*, 741

Synthesis of carboxylic acid esters from α-ketocarboxylic acid esters via α-hydroxycarboxylic acid esters COCOOR → CHR′COOR
s. *8*, 720

Tert. alcohols from carboxylic acid esters COOR → C(OH)R$_2$

Cyclic tert. alcohols
s. *7*, 695

Amino-tert-alcohols
Use of Trilon B in Grignard reactions
s. *9*, 742

Synthesis of hydroxyketones from ketocarboxylic acid esters
Blocking of keto groups by formation of acetals
s. *9*, 743

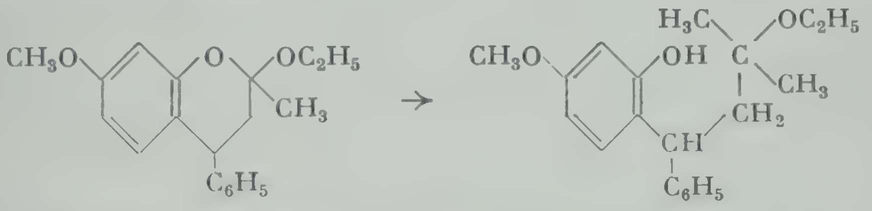
Enollactols from enollactones ←
s. *8*, 884

Synthesis of long-chain α,ω-dicarboxylic acids ←
Carboxylic acids from dicarboxylic acid imides
via α-hydroxylactams and ketocarboxylic acids
s. *9*, 744

Lactones from ketocarboxylic acid esters C
s. *7*, 696; phthalides s. *8*, 721

Phenols from chromans C

2.



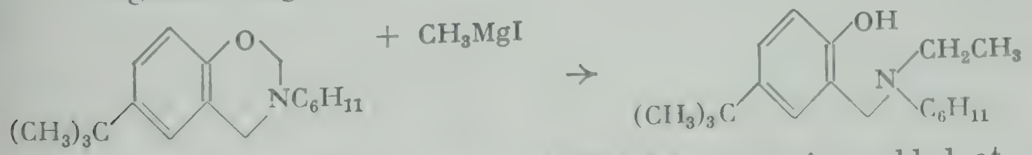
A soln. of 2-ethoxy-7-methoxy-2-methyl-4-phenylchroman in dry ether slowly added to a rapidly stirred soln. of methyl-MgI in ether, and refluxed 10 hrs. with stirring → 2-ethoxy-4-(2-hydroxy-4-methoxyphenyl)-2-methyl-4-phenylbutane. Y: 88%. D. W. Clayton et al., Soc. *1953*, 581.

Diols from lactones – Coumarin ring opening
s. *7*, 815

Hydroxyketones from lactones
s. *6*, 687

Ketocarboxylic acids from dicarboxylic acid anhydrides
Inverse Grignard reaction s. *8*, 722

3,4-Dihydro-2H-1,3-benzoxazine ring opening with Grignard reagents



3,4-Dihydro-3-cyclohexyl-6-*tert*-butyl-2H-1,3-benzoxazine added at −5 to 5° to a 2-4 fold excess of ethereal methyl-MgI, then refluxed for a brief period before isolating the product → 2-(N-cyclohexyl-ethyl-

aminomethyl)-4-*tert*-butylphenol. Y: 82.2%. F. e. s. K. G. Mizu
Ж. *23*, 861 (1953); C. A. *48*, 3982f.

Magnesium/mercuric halide *Mg/HgI*

Synthesis with CO → C(OH)C·CO
halogenocarboxylic acid esters and oxo compounds
Extended Reformatskii synthesis
s. *8*, 723

Magnesium/mercuric bromide *Mg/Hg*

Pinacols
s. *7*, 697

Zinc

Reformatskiĭ synthesis

524. In cases where ethyl α-bromopropionate gives a poor yield due to se condensation or other side-reactions the use of isobutyl α-bromopr pionate may improve the yield. M. S. Newman and F. J. Evans, J Am. Soc. *77*, 946 (1955).

s. a. *9*, 373; C. D. Gutsche and F. A. Fleming, Am. Soc. *76*, 1771 (195

of acetylenealcohols from oxo compounds CO → C(OH)C⋮C
s. *6*, 688; allenes as by-products s. L. Crombie and A. G. Jackli Soc. *1955*, 1740

of carboxylic acids from ketones
Synthesis with addition of 2 C-atoms
Reductive hydrolysis
s. *7*, 699

of carboxylic acid esters
Dehydration with simultaneous esterification
s. *6*, 689

of β-hydroxycarboxylic acid esters CHO → CH(OH)C·COO
from aldehydes
s. *7*, 700

Alkylmagnesium bromide *RMgB*

β-Hydroxycarboxylic acids from oxo compounds CO → C(OH)C·COO
s. *7*, 701

Ethylmagnesium bromide C_2H_5MgB

Acetylenealcohols from oxo compounds CO → C(OH)C⋮C
s. *6*, 686

Synthesis of hydroxysulfones from oxo compounds CO → C(OH)
s. *9*, 745

Phenylmagnesium bromide C_6H_5MgB

Tert. alcohols from ketones
Polyfluoro compounds s. *9*, 746

Diethylaminomagnesium bromide *$(C_2H_5)_2NMgBr$*

β-Hydroxycarboxylic acid esters from ketones CO → C(OH)C·COOR

s. *9*, 747

Methylanilinomagnesium bromide *$C_6H_5N(CH_3)MgBr$*

β-Hydroxyketones C(OH)·C·CO

s. *8*, 724

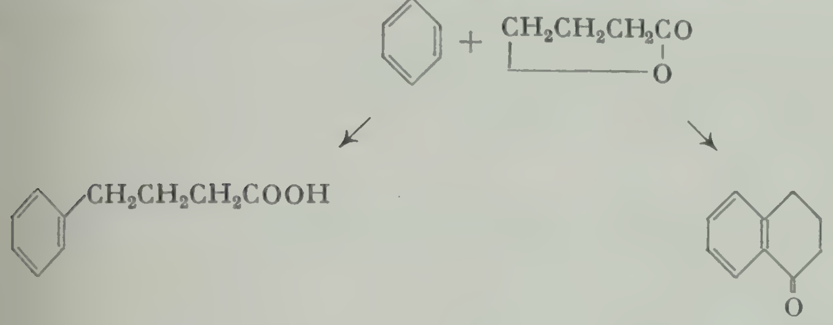
Aluminum chloride *$AlCl_3$*

Prim. alcohols from oxido compounds

s. *9*, 748

Synthesis of carboxylic acids and cyclic ketones from lactones

5.

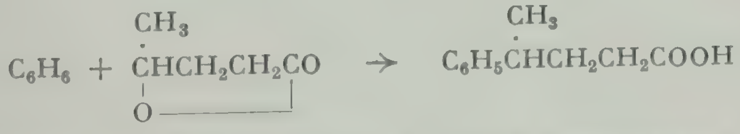


0.3 mole	0.6 mole

$AlCl_3$ added during ca. 1 hr. to a well-stirred soln. of benzene and γ-butyrolactone at a rate that keeps the soln. refluxing, and refluxing continued ca. 4 hrs. until the HCl-evolution has nearly ceased →

γ-phenylbutyric acid (Y: 73%) and α-tetralone (Y: 11%).	α-tetralone. Y: 66%.

W. E. Truce and C. E. Oson, Am. Soc. *74*, 4721 (1952); improved yield of α-tetralone and 4-methyl-1-tetralone s. Org. Synth. *35*, 95 (1955); condensation with $AlCl_3$ followed by ring closure with polyphosphoric acid s. W. L. Mosby, J. Org. Chem. *18*, 964 (1953).



$$C_6H_6 + \underset{O}{\overset{CH_3}{C}}HCH_2CH_2CO \rightarrow C_6H_5\overset{CH_3}{C}HCH_2CH_2COOH$$

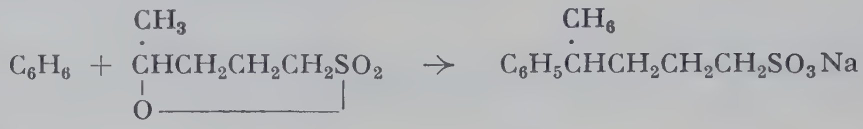
γ-Valerolactone added dropwise to a stirred suspension of $AlCl_3$ in benzene, and heated 30 min. on a water bath → γ-phenylvaleric acid. Y: 61%.—No isomerization of the side chain takes place and the phenyl radical is attached at the position of the alcohol function in the parent hydroxy acid. F. e. s. R. V. Christian, Jr., Am. Soc. *74*, 1591 (1952); s. a. A. Müller and M. Vajda, J. Org. Chem. *17*, 800 (1952); E. M. Fry, J. Org. Chem. *17*, 1484 (1952); D. D. Phillips and A. W. Johnson, Am. Soc. *77*, 5977 (1955).

Ketocarboxylic acids from dicarboxylic acid anhydrides
s. *1*, 519; *2*, 601; *3*, 566; *4*, 635a; s. a. D. N. Chatterjee, Am. Soc. *77*, 513 (1955)

with migration of a carbon-carbon double bond
s. *6*, 690

Reactions and syntheses with sultones

527.



$$C_6H_6 + \underset{|\,O\,\text{————}|}{\overset{CH_3}{\dot{C}}}HCH_2CH_2CH_2SO_2 \rightarrow C_6H_5\overset{CH_3}{\dot{C}}HCH_2CH_2CH_2SO_3Na$$

Synthesis of sulfonic acids. $AlCl_3$ added portionwise with stirring during ca. 0.5 hr. to 4-hydroxy-1-pentanesulfonic acid sultone and benzene as rapidly as it dissolves, heated 6.5 hrs. at 80° and the product isolated as the Na-salt → Na-4-phenyl-1-pentanesulfonate. Y: 88%. F. e s. W. E. Truce and F. D. Hoerger, Am. Soc. *76*, 5357 (1954); f. reactions and syntheses s. Am. Soc. *77*, 2496 (1955).

Cyanohydrins ←

Hydroxyketones from diketones via ketocyanohydrins ←
Protection of keto groups
by formation of enolethers and ketals
Cyanohydrins by interchange
s. *8*, 725

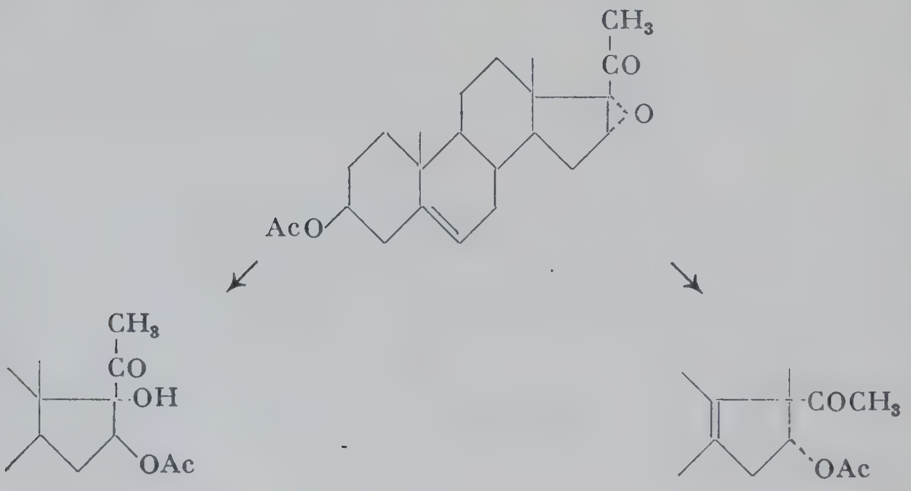
Amberlite ←

Catalysis with anion exchange resins ←
Nitroalcohols from nitroparaffins and aldehydes
Cyanoethylation
s. *9*, 749

p-Toluenesulfonic acid *TsOH*

Glycol monoesters and rearranged acoxyethylenes ←
from oxido compounds – Steroids

528.



Δ^5-3β-Acetoxy-16,17α-oxido-20-ketopregnene,

500 mg., in glacial acetic acid containing H_2SO_4 allowed to stand 6 hrs. at room temp. → 310 mg. Δ^5-17α-hydroxy-3β,16β-diacetoxy-20-ketopregnene.—Other methods were not successful.

5.0 g., refluxed 3 hrs. in acetic anhydride containing p-toluenesulfonic acid monohydrate at a bath temp. of 170°, anhydrous K-acetate added, and evaporated in vacuo → 3.02 g. $\Delta^{5,13}$-3β,16α-diacetoxy-17β-methyl-18-nor-20-keto-17α-pregnadiene.

F. glycol monoesters s. K. Heusler and A. Wettstein, B. *87*, 1301 (1954).

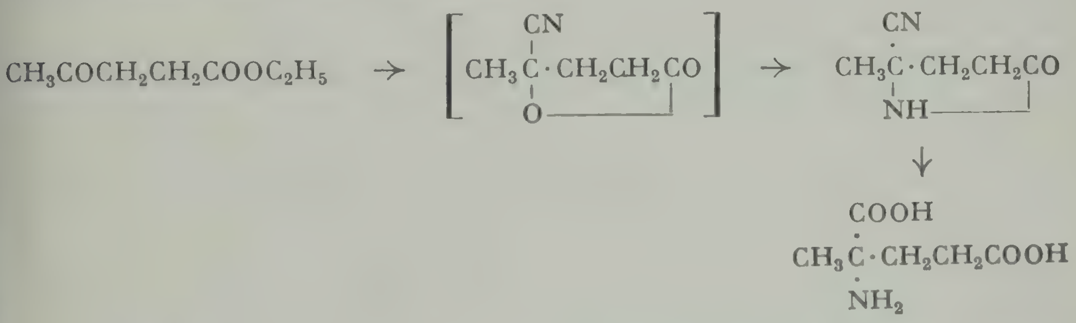
Sulfuric acid *H_2SO_4*

Cyanohydrins from ketones CO → C(OH)CN

s. *8*, 727

Ammonium chloride *NH_4Cl*

α-Aminodicarboxylic acids from ketocarboxylic acid esters via cyanolactones and cyanolactams ←



A soln. of ethyl levulinate in ethanol added to an aq. soln. of NH_4Cl and KCN, allowed to stand 24 hrs. at room temp., aq. 28%-NH_3 added, and allowed to stand for an additional 24 hrs. → γ-cyano-γ-valerolactam (Y: 73%) refluxed 2 hrs. in 38%-HBr → dl-α-methylglutamic acid (Y: 85%). Also isolation of the lactone s. A. E. Gal, S. Avakian, and G. J. Martin, Am. Soc. *76*, 4181 (1954).

Cobalt carbonyl *$Co(CO)_4$* ←

Homologation of alcohols

s. *9*, 750

Nickel carbonyl *$Ni(CO)_4$*

Carboxylic acids from alcohols C·OH → C·COOH

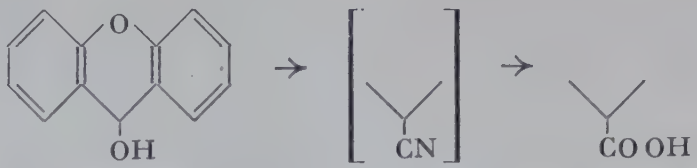
Synthesis with addition of 1 C-atom

by carbonylation

s. *7*, 702

Via intermediates *v.i.*

530.



A mixture of xanthydrol, NaCN, and glacial acetic acid heated 24 hrs. at 100° in an autoclave, and the crude product refluxed 24 hrs. with KOH in 75%-methanol → xanthene-9-carboxylic acid. Y: 68-69%. W. S. Ide, E. Lorz, and R. Baltzly, Am. Soc. *76*, 1122 (1954).

Addition to Nitrogen and Carbon CC ⇓ NC

Without additional reagents *w.a.r.*

α-Hydroxylaminonitriles from oximes C:NOH → C(CN)NHOH
s. *8*, 728

α-Cyanohydrazines from hydrazones N:C → NHC·CN
s. *9*, 751

Nitramines from azomethines and nitroparaffins ←
s. *7*, 703

Reactions with nitroacetic ester ←
s. *9*, 856

1-Acyl-1,2-dihydroquinaldonitriles (Reissert compounds) from carboxylic acid chlorides ←
s. *6*, 122

Azacyclopropanes from O-alkoximes via 1,2,3-triazolines ○
s. *7*, 704

Potassium hydroxide *KOH*

Nitramines from cyclic quaternary ammonium salts via pseudobases ←
s. *7*, 705

n-Butyllithium n-C_4H_9Li

(Hindered) ketimines from nitriles CN → C(:NH)R
s. *9*, 752

Potassium carbonate K_2CO_3

α-Nitrocarboxylic acid amides from isocyanates N:C:O → NHCOR
s. *9*, 753

Potassium cyanide *KCN*

Hydantoins from imines ○
s. *9*, 754

Diethylamine $(C_2H_5)_2NH$

1,2-Nitramines from azomethines N:C → NHCR
s. *9*, 413

Triethylamine $(C_2H_5)_3N$

(Hydroxyaryl)arylenediamides from quinone diimides ←
s. *8*, 729

Pyridine C_5H_5N

Cyanoformamides from isocyanates N:C:O → NHCOCN
s. *6*, 691

Magnesium *Mg*

Sec. amines from azomethines C:NR → C(NHR)R′
s. *4*, 643; s. a. R. Paul and S. Tchelitcheff, Bl. *1953*, 1014

4-Subst. 1,4-dihydroquinolines from quinolines ←
s. *8*, 730

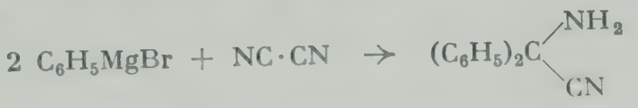
Ketimines from nitriles CN → C(:NH)R
s. *7*, 706; s. a. F. A. Vingiello, A. Bořkovec, and J. Schulman, Am. Soc. *77*, 2321 (1955); C. R. Hauser and D. S. Hoffenberg, Am. Soc. *77*, 4885 (1955)

Ketones from nitriles CN → COR
s. *1*, 523/4; *2*, 605, 699; *4*, 644/5; also side-reactions with perfluoronitriles s. E. T. McBee, O. R. Pierce, and D. D. Meyer, Am. Soc. *77*, 917 (1955)

Synthesis of azomethines from nitriles ←
s. *9*, 756

Reaction of cyanogen with Grignard reagents ←
α-Aminonitriles from halides and cyanogen

31.



$$2\ C_6H_5MgBr + NC{\cdot}CN \rightarrow (C_6H_5)_2C\begin{matrix}NH_2\\ CN\end{matrix}$$

Cyanogen allowed to react with a soln. of phenyl-MgBr in ether, warmed gently on a water bath for 30 min., allowed to stand overnight, then hydrolyzed with satd. NH_4Cl-soln. → diphenylglycinonitrile (startg. m. f. 221). Y: ca. 33%. F. e. s. H. M. Woodburn and L. B. Lathroum, J. Org. Chem. *19*, 285 (1954).

Subst. carboxylic acid thioamides from isothiocyanates N:C:S → NHC(:S)R
s. *6*, 692

Endopyrimidine ring from α,β-ethylenenitriles ○
s. *9*, 755

Magnesium/lithium aluminum hydride *Mg/LiAlH₄*
s. Lithium aluminum hydride/magnesium

Diisopropylaminomagnesium bromide R_2NMgBr

β-Iminonitriles from 2 nitrile molecules ←
s. *7*, 707

Pyrimidines from 3 nitrile molecules ○
s. *7*, 708

Zinc *Zn*

β-Ketocarboxylic acid esters from nitriles CN → COC·COOR

Blaise reaction

s. *10*, 244; s. a. J. Cason, K. L. Rinehart, Jr., and S. D. Thornton, Jr., J. Org. Chem. *18*, 1594 (1953); in the presence of a little $CuBr_2$ s. K. L. Rinehart, Org. Synth. *35*, 15 (1955)

Lithium aluminum hydride/magnesium *$LiAlH_4/Mg$*

Synthesis of amines from nitriles ←

s. *9*, 756

Aluminum chloride *$AlCl_3$*

Aminoketones from aminonitriles CN → COR

Hoesch synthesis

s. *6*, 693; s. a. E. D. Hornbaker and A. Burger, Am. Soc. *77*, 5314 (1955)

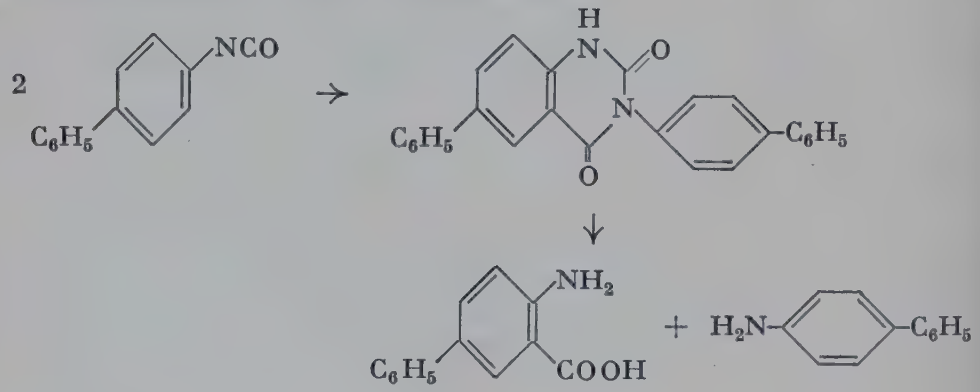
2-Aryl-p-phenylenedisulfonamides from p-quinone disulfonimides ←

s. *7*, 709

Aluminum chloride/sodium chloride *$AlCl_3/NaCl$*

o-Aminocarboxylic acids from isocyanates via 2,4-dioxo-1,2,3,4-tetrahydroquinazolines ←

532.



Ar. isocyanates and their dimers with a molten mixture of $AlCl_3$ and NaCl yield 3-aryl-2,4-dioxo-1,2,3,4-tetrahydroquinazolines. These decompose on heating with aq. alkali into ar. amines and the corresponding o-aminoacids. The reaction is useful for the introduction of carboxyl in o-position to an NH_2-group.—E: p-Biphenyl isocyanate added at 135-140° to molten $AlCl_3$-NaCl, stirred 30 min., and the crude product boiled with 10%-NaOH → 2-amino-5-phenylbenzoic acid. Y: 65.5%. F. e. s. N. S. Dokunikhin and L. A. Gaeva, Ж. *23*, 606 (1953); C. A. *48*, 7018f.

Amberlite (cyanide form) ←

Catalysis with anion exchange resins ←

Cyanohydrins and benzoins

s. *8*, 731

Acetic acid *CH_3COOH*

Carbacoxyamines from azomethines ←

s. *7*, 710

Sulfur trioxide/dioxane ←

Sym. oxalic acid amides from isonitriles ←

s. *8*, 732

Sulfuric acid *H_2SO_4*

3,4-Dihydroisoquinolines from nitriles ○

New synthesis s. *9*, 757

Hydrochloric acid *HCl*

Hydrazodinitriles from cyanohydrazones ←

s. *8*, 797

Addition to Sulfur and Carbon CC⇓SC

Without additional reagents *w.a.r.*

1,2,3-Thiadiazoles from isothiocyanates and diazomethane ○

s. *6*, 694

Magnesium *Mg*

Dithiocarboxylic acid esters from halides and carbon disulfide ←

s. *8*, 733

Addition to Carbon CC⇓CC

Without additional reagents *w.a.r.*

4-Subst. 1,4-dihydropyridines from pyridines ←

s. *8*, 734

Synthesis of polyhalides ←

s. *9*, 758; s. a. Soc. *1955*, 3005

Reaction of oxalyl chloride with unsatd. compounds ←

α,β-Ethylenecarboxylic acids from ethylene derivatives

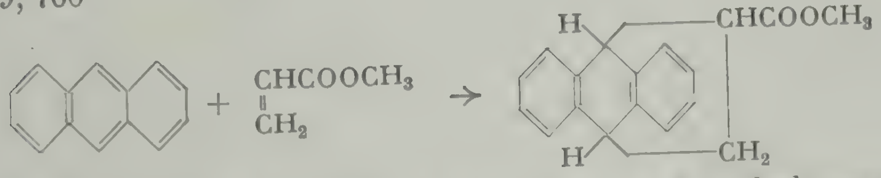
s. *9*, 759

Diene synthesis – Diels-Alder reaction ○

Linear annulization

s. *9*, 760

33.



with anthracenes. A mixture of anthracene and methyl acrylate in xylene heated 12 hrs. at 210° in a steel bomb → 9,10-dihydro-9,10-(11-carbomethoxyethano)anthracene. Y: 93%. F. e. s. S. Wawzonek and J. V. Hallum, J. Org. Chem. *18*, 288 (1953).

with unsym. addends; with carboxylic acid chlorides
Steric effects s. *7*, 711

with nitro compounds
s. *9*, 299

Isocyclics from acetylene derivatives
s. *7*, 712; *8*, 735

Diene synthesis via enolesters
Polymerization inhibitors s. *6*, 695

Dihydropyrans from α,β-ethyleneoxo compounds
s. *6*, 696

Dimers by polymerization reaction
s. *6*, 697

Azetidinones
s. *8*, 736

Pyrazolines from ethylene derivatives and diazo compounds

Pyrazoles via nitropyrazolines
s. *7*, 713

3-Halogeno- and 3-nitro-pyrazoles
from 1-nitro-1,2-ethylene-1-halides
s. *8*, 737

Isoxazolines from nitrile oxides
s. *7*, 714

Irradiation ←

Free radical additions – Synthesis of polyhalides C:C → CHalCR
s. *9*, 761; s. a. R. N. Haszeldine and B. R. Steele, Soc. *1955*, 3005

Photodimerization
Cyclobutane ring from ethylene derivatives ○
s. *6*, 698

Electrolysis ↯

Alkoxylation of furans ←
s. *9*, 762

Lithium *Li*

o-Aryl dihydroaryl ketones from aryl ketones C:C → CHCR
s. *7*, 715

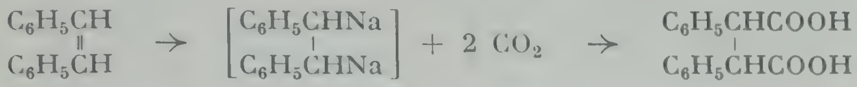
Sodium *Na*

C-Cyanoethylation H → CH_2CH_2CN
s. *9*, 763

Pyridylethylation C:C → CHCR
s. *7*, 716; *9*, 764

Reactions with organo-1,2-dimetallic compounds ←
Succinic acids from ethylene derivatives

34.



$$\begin{matrix}C_6H_5CH\\ \Vert\\ C_6H_5CH\end{matrix} \rightarrow \left[\begin{matrix}C_6H_5CHNa\\ |\\ C_6H_5CHNa\end{matrix}\right] + 2\ CO_2 \rightarrow \begin{matrix}C_6H_5CHCOOH\\ |\\ C_6H_5CHCOOH\end{matrix}$$

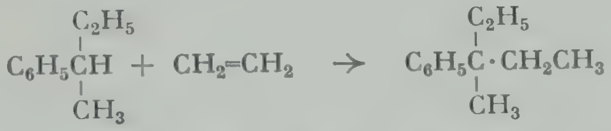
Stilbene allowed to react with Na in *1,2-dimethoxyethane* during 2 hrs., then the liquid drained from the unused metal through a stopcock into Dry Ice, finally treated with water → crude *meso*-diphenylsuccinic acid (Y: ca. 70%) and a small amount of the d,l-isomer (Am. Soc. *61*, 2106).—Tetrahydrofuran can be used as solvent in place of 1,2-dimethoxyethane (J. Org. Chem. *18*, 447). F. e. s. G. F. Wright, Am. Soc. *61*, 2106 (1939); A. G. Brook, H. L. Cohen, and G. F. Wright, J. Org. Chem. *18*, 447 (1953).

Sodium/o-Chlorotoluene ←

α-Ethylation of side chains

H → CH_2CH_3

35.



$$\begin{matrix}C_2H_5\\ |\\ C_6H_5CH\\ |\\ CH_3\end{matrix} + CH_2{=}CH_2 \rightarrow \begin{matrix}C_2H_5\\ |\\ C_6H_5C\cdot CH_2CH_3\\ |\\ CH_3\end{matrix}$$

sec-Butylbenzene heated 4 hrs. with Na and some o-chlorotoluene as promoter in a rotating autoclave under an initial ethylene pressure of 30 atm. at 200-225° → 3-methyl-3-phenylpentane. Y: 90%.–Compounds capable of reacting with Na to form organo-Na-compounds are used as promoters. F. e. s. H. Pines, J. A. Vesely, and V. N. Ipatieff, Am. Soc. *77*, 554 (1955).

NaOH

Sodium hydroxide

C-Cyanoethylation

H → CH_2CH_2CN

of aldehydes s. *9*, 768

NaOH/C₅H₅N

Sodium hydroxide/pyridine

s. *7*, 717

KOH

Potassium hydroxide

s. *6*, 699

Subst. propionic acids from carboxylic acid esters via α-(2-cyanoethyl)carboxylic acid esters

s. *6*, 700

Potassium hydroxide/alcohol

C-Cyanoethylation

of α-cyanocarboxylic acid esters s. *6*, 701
of 1,1-disulfones s. *9*, 767

Aliphatic β-dinitro compounds ←

s. *6*, 702

Potassium hydroxyide/acetal *$KOH/RCH(OR')_2$*

Syntheses with potassium hydroxide in solvents of the acetal type ←

Michael addition
s. *7*, 718

Sodium/alcohol *NaOR*

Michael addition ←

with alkylmalonic esters
s. *8*, 738; also "abnormal" Michael addition s. G. A. Swan, Soc. *1955*, 1039

Cyclobutanes
s. *8*, 739

Cyclohexanediones
s. *6*, 703

followed by Fischer indole synthesis
s. *8*, 740

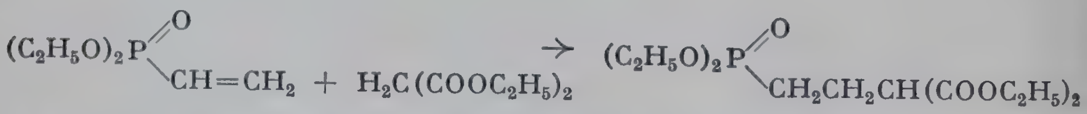
C-Cyanoethylation H → CH_2CH_2CN
s. *7*, 719

with simultaneous formation of ketocarboxylic acid esters from cyclic β-diketones
s. *10*, 141

γ-Cyanoketones and δ-ketocarboxylic acids from β-ketocarboxylic acid esters via α-cyanoethyl-β-ketocarboxylic acid esters
s. *9*, 765

Phosphonoethylation ←

536.



$$(C_2H_5O)_2P\begin{matrix}\nearrow O\\ \searrow CH{=}CH_2\end{matrix} + H_2C(COOC_2H_5)_2 \rightarrow (C_2H_5O)_2P\begin{matrix}\nearrow O\\ \searrow CH_2CH_2CH(COOC_2H_5)_2\end{matrix}$$

A soln. of Na in ethanol added dropwise during 10-15 min. to a mixture of diethyl vinylphosphonate and diethyl malonate until reaction ceases, and allowed to stand 1 hr. at room temp. → diethyl γ-dicarbethoxypropylphosphonate. Y: 79.6%. F. e. s. A. N. Pudovik and O. N. Grishina, Ж. *23*, 267 (1953); C. A. *48*, 2573c and other papers of this series.

2-Pyrones from α,β-acetyleneketones ○
s. *7*, 720

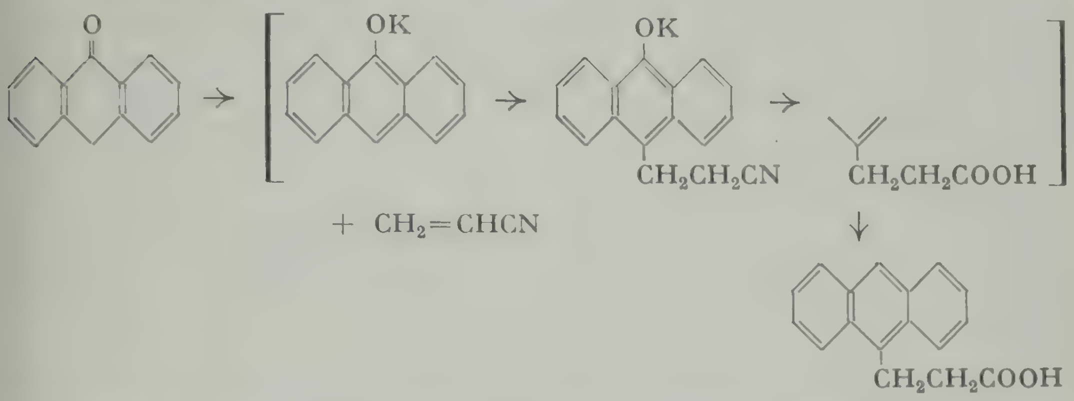
Cyclopentanones from cyclopropanes ←
s. *9*, 766

Potassium tert-butoxide *KOR*

Michael addition – Syntheses with benzyl esters ←
s. *8*, 741

C-Monocyanoethylation H → CH_2CH_2CN
Carboxylic acids from nitriles
Replacement of hydroxyl by hydrogen

7.



Anthrone dissolved in a soln. of K in *tert*-butanol, stirred 1 hr. at room temp., then treated dropwise during 1 hr. with a soln. of acrylonitrile in *tert*-butanol, refluxed 2 hrs., aq. HCl added, the crude oily nitrile separated and refluxed 2 hrs. with concd. HCl, the crude acid dissolved in aq. NH_3 and heated 4 hrs. at 90-95° with Zn-dust activated with Cu-sulfate → β-(9-anthranyl)propionic acid (startg. m. f. 65). Y: 90-95%. G. H. Daub and W. C. Doyle, Am. Soc. *74*, 4449 (1952).

Sodium amide *$NaNH_2$*

α,β-Ethylene-δ-ketocarboxylic acid esters ←
from ketones and propiolic esters
s. *6*, 704

Alkali cyanide ←

Subst. succinic acids C:C → CHC(CN)
Dicarboxylic acids from dicyanocarboxylic acid esters

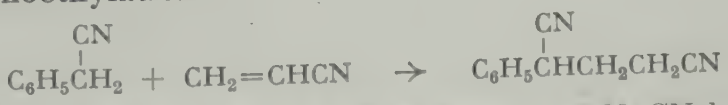
with KCN s. *6*, 705; s. a. D. N. Chatterjee, Am. Soc. *77*, 414 (1955); condensation with commercial pyridine and hydrolysis over a period of 45-50 hrs. s. P. B. Talukdar and P. Bagchi, J. Org. Chem. *20*, 21 (1955)

NaCN

Sodium cyanide

C-Monocyanoethylation H → CH_2CH_2CN

8.



$$C_6H_5\overset{CN}{\overset{|}{C}}H_2 + CH_2{=}CHCN \rightarrow C_6H_5\overset{CN}{\overset{|}{C}}HCH_2CH_2CN$$

Excess phenylacetonitrile and a small amount of NaCN heated in an oil bath to 225°, a little water then acrylonitrile added dropwise with stirring, which is continued for 30 min. at the same temp. → α-phenylglutaronitrile. Y: 65%. A. D. Campbell, Soc. *1954*, 1377.

KCN

Potassium cyanide

C-Cyanoethylation of aldehydes
s. *9*, 768

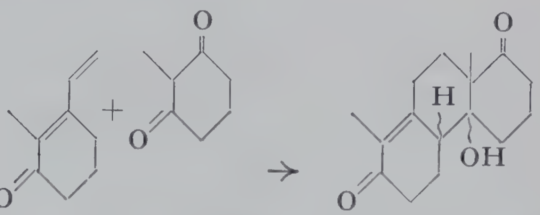
1,2-Dinitriles C(CN)C(CN
from α,β-ethylene-α-cyanocarboxylic acid esters
s. *3*, 583; s. a. J. Harley-Mason and A. H. Jackson, Soc. *1954*, 3651

Triton B ←
C-Cyanoethylation $H \rightarrow CH_2CH_2C$
Carboxylic acids from nitriles
Blocking of ketone α-positions
s. *9*, 769

Triton B and Benzyltrimethylammonium butoxide ←
Aliphatic nitro compounds from ethylene derivatives C:C → CHC
s. *7*, 721

Diethylamine *$(C_2H_5)_2NH$*
Dodecahydrophenanthrene ring

539.



2-Methyl-3-vinyl-2-cyclohexen-1-one, 1-methyl-2,6-cyclohexanedione, anhydrous diethylamine, abs. *tert*-butanol, and benzene heated 110 hrs. at 110-130° in a sealed tube → 8,10a-dimethyl-1,7-dioxo-4a-hydroxy-Δ^8-dodecahydrophenanthrene. Y: 42%. A. Eschenmoser, J. Schreiber, and S. A. Julia, Helv. *36*, 482 (1953).

Pyridine ring from cyanoacetamides
s. *6*, 706

Pyridine/sodium hydroxide s. Sodium hydroxide/pyridine *$C_5H_5N/NaOH$*

Cuprous chloride *CuCl*
Synthesis of 3-amino-1-butynes ←
s. *6*, 707

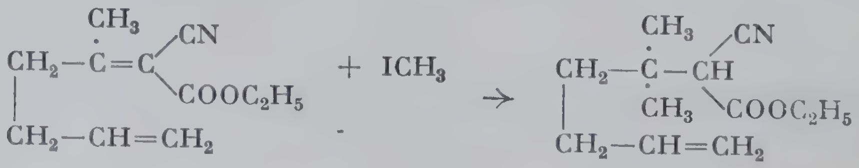
Cuprous halide/magnesium s. Magnesium/cuprous halide *CuHal/Mg*

Calcium hydride/methyl alcohol *CaH_2/CH_3OH*
Aliphatic nitro compounds from ethylene derivatives C:C → CHCR
s. *7*, 722

Calcium carbide/nickel acetylacetonate ←
s. Nickel acetylacetonate/calcium carbide

Magnesium *Mg*
Addition of Grignard reagents to carbon-carbon double bonds
s. *9*, 770

540.



$$\begin{array}{l} CH_2-\overset{CH_3}{C}=C{<}^{CN}_{COOC_2H_5} \\ | \\ CH_2-CH=CH_2 \end{array} + ICH_3 \rightarrow \begin{array}{l} CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH{<}^{CN}_{COOC_2H_5} \\ | \\ CH_2-CH=CH_2 \end{array}$$

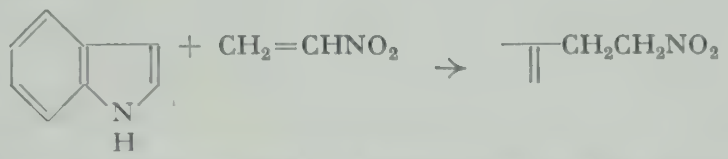
Selective addition. Ethyl 1-methyl-4-n-pentenylidenecyanoacetate in dry ether added to ethereal methyl-MgI at such a rate as to maintain gentle reflux, and stirred ¼ hr. after complete addition → ethyl 1,1-dimethyl-4-n-pentenylcyanoacetate (startg. m. f. 679). Y: 77%. F. e. s. E. van Heyningen, Am. Soc. *76*, 2241 (1954); addition to α,β-ethylene-α-cyanocarboxylic acid esters s. a. F. S. Prout et al., Org. Synth. *35*, 6 (1955).

Synthesis of hydrocarbons from ethylene derivatives
s. *8*, 743

Synthesis of β,γ-ethylenecarboxylic acids from α-allenecarboxylic acids and of carboxylic acids from α,β-ethylenecarboxylic acids
s. *9*, 771

C-Nitroethylation H → $CH_2CH_2NO_2$

1.



An ethereal soln. of nitroethylene added slowly with vigorous stirring to an ice-cooled soln. of indole-MgI, prepared from indole, Mg-turnings, and ethyl iodide in ether according to J. W. Baker, Soc. *1946*, 461, stirred 1 hr. at room temp., finally refluxed 0.5 hr. → 3-(2-nitroethyl)-indole. Y: 28%. W. E. Noland and P. J. Hartman, Am. Soc. *76*, 3227 (1954).

Hydrolytic ring opening of isocyclics with simultaneous formation of ethylene derivatives from sulfonic acid esters ←
s. *9*, 772

Magnesium/cuprous halide *Mg/CuHal*

Synthesis of ketones from α,β-ethyleneketones C:C → CHCR
1,4-Addition
with CuCl s. *8*, 742; optimum amount of CuCl, also 1,2-addition s. G. Chiurdoglu and A. Maquestian, Bl. Soc. chim. Belg. *63*, 357 (1954); with CuBr s. *1*, 536; s. a. G. Clément, Bl. *1954*, 228

Mercuric chloride/arsenic trichloride *$HgCl_2/AsCl_3$*
s. Arsenic trichloride/mercuric chloride

Aluminum amalgam *Al,Hg*

Reductive dimerization ←
s. *9*, 773

Boron fluoride *BF_3*

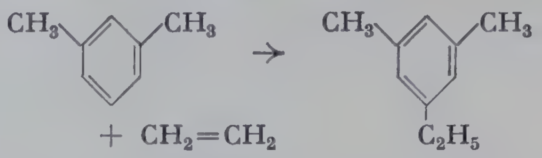
1,3-Diol ethers from ethylene derivatives and acetals ←
s. *9*, 774

β-Alkoxyacetals from enolethers ←
s. *7*, 724

Boron fluoride/hydrogen fluoride *BF_3/HF*

Alkylation of arenes with olefins ArH → ArR

542.



Ethylene added during 1 hr. at 62° to a mixture of m-xylene, HF, and BF_3 → 1,3,5-ethylxylene. Y: ca. 80%.—The presence of very strong acids, as HF-BF_3, favors the formation of single isomers. D. A. McCaulay and A. P. Lien, Am. Soc. *77*, 1803 (1955).

Aluminum chloride *$AlCl_3$*

Synthesis of hydrocarbons from ethylene derivatives C:C → CHCR
Eijkman reaction

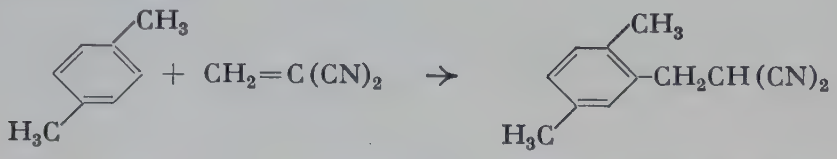
s. *4*, 659; s. a. J. O. Jílek, V. Šimák, and M. Protiva, Coll. Czech. Chem. Communs. *19*, 298 (1954)

Synthesis of hydrocarbons from ethylene derivatives with exchange of C-aryl groups ←

s. *8*, 875

2-Aryl-1,1-dinitriles ←

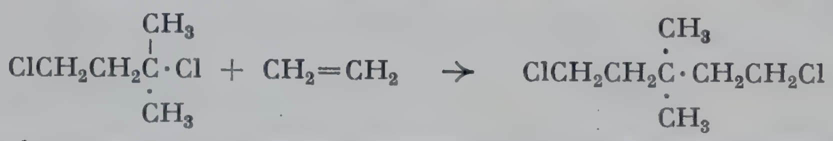
543.



A soln. of p-xylene and vinylidene cyanide in *sym*-tetrachloroethane added dropwise at 20-25° to a stirred suspension of anhydrous $AlCl_3$ in the same solvent, and the product isolated after 15 min. → 2,5-dimethylbenzylmalononitrile. Y: 79.4%. F. e. s. J. C. Westfahl and T. L. Gresham, Am. Soc. *76*, 1076 (1954).

Synthesis of halides from ethylene derivatives C:C → CHalCR

544.



$$\mathrm{ClCH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}\cdot Cl + CH_2{=}CH_2 \rightarrow ClCH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}\cdot CH_2CH_2Cl}$$

Ethylene bubbled into a stirred mixture of 1,3-dichloro-3-methylbutane (prepn. s. 418) and $AlCl_3$, the temp. permitted to rise from ca. –60° to –15° where the reaction starts, and kept at –15 to –10° for 4 hrs. → 1,5-dichloro-3,3-dimethylpentane (startg. m. f. 200, 355). Y: 68%. F. e. s. L. Schmerling and J. P. West, Am. Soc. *74*, 2885 (1952).

β-Chloroketones from carboxylic acid chlorides ←

s. *7*, 725; s. a. W. M. McLamore, S. Y. P'An, and A. Bavley, J. Org. Chem. *20*, 109 (1955)

Hydroximinochlorides from α,β-nitroethylene derivatives ←

s. *7*, 726

Diethylamine acetate ←

Benzene ring by trimerization ○
s. *9*, 775

Acetic anhydride $(CH_3CO)_2O$

Nitriles from ethylene derivatives C:C → CHC(CN)
s. *9*, 776

Ar. carboxylic acid anhydrides ○
by dimerization of α,β-acetylenecarboxylic acids
s. *4*, 661; s. a. A. D. Campbell, Soc. *1954*, 3659

Benzoyl peroxide $(C_6H_5COO)_2$

Free radical reactions ←
Synthesis of ketones from aldehydes and ethylene derivatives
s. *8*, 745; from perfluoroölefins, also synthesis of alcohols, s. J. D. Lazerte and R. J. Koshar, Am. Soc. *77*, 910 (1955)

Polyhalides ←
s. *7*, 727

Acetic acid CH_3COOH

Pyridine ring synthesis ○
4-Azafluorenones s. *6*, 709

Aryl mercaptans $ArSH$

Reductive dimerization ←
s. *10*, 72

o-Chlorotoluene/sodium s. Sodium/o-chlorotoluene ←

Titanium tetrachloride $TiCl_4$

C-Alkylation with ethylene derivatives C:C → CHCR
s. *10*, 630

Triphenylphosphine $(C_6H_5)_3P$
s. under cobalt and nickel carbonyls

Arsenic trichloride $AsCl_3$

Dimerization ←
s. *7*, 723

Arsenic trichloride/mercuric chloride $AsCl_3/HgCl_2$

with simultaneous ring closure ○
s. *7*, 723

Sulfur dioxide SO_2

Heterocyclic ketones from α,β-ethyleneketones C:C → CHCR
s. *7*, 728

Alkanesulfonic acids RSO_3H

Alkenylation of aryl derivatives ←
with migration of a carbon-carbon double bond
s. *7*, 729

Sulfuric acid H_2SO

Indan ring by dimerization ○
s. *8*, 746; s. a. M. J. Rosen, Org. Synth. *35*, 83 (1955)

m-Dioxanes from ethylene derivatives
s. *4*, 637

Alcohols from ethylene derivatives via m-dioxanes
Synthesis with addition of 1 C-atom
s. *7*, 730

Chromium oxide/alumina Cr_2O_3/Al_2O_3

Pyridine ring from dienes
s. *9*, 777; cf. Am. Soc. *77*, 3014, 3143 (1955)

Hydrogen fluoride HF

Isomerization accompanying alkylation of arenes ←
s. *8*, 747

One-step indanone ring synthesis ○
s. *6*, 819

Ferrous sulfate $FeSO_4$

Diketones from hydroperoxides – Dimerization ←
s. *7*, 731

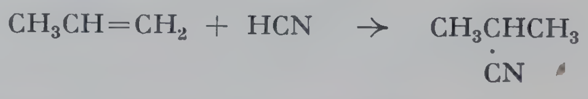
Cobalt-silica and cobalt $Co\text{-}SiO_2$ *and Co*

Carboxylic acid esters from ethylene derivatives C:C → CHC(COOR)
Synthesis with addition of 1 C-atom
s. *8*, 748

Cobalt carbonyl/triphenylphosphine $Co(CO)_4/(C_6H_5)_3P$

Nitriles from ethylene derivatives C:C → CHC(CN)

545.



$$CH_3CH{=}CH_2 + HCN \rightarrow \underset{CN}{CH_3CHCH_3}$$

Propylene heated with hydrogen cyanide in the presence of dicobalt octacarbonyl and triphenylphosphine at 130° and 100 atm. for 14.5 hrs. whereby at 70° the reaction flashed to 183° and 300 atm. → isobutyronitrile. Conversion: 75%. F. e. s. P. Arthur, Jr., et al., Am. Soc. *76*, 5364 (1954).

Nickel acetylacetonate/calcium carbide ←

Subst. cyclooctatetraenes by copolymerization ○
s. *9*, 778

Nickel carbonyl $Ni(CO)_4$

α,β-Ethylenecarboxylic acids from acetylene derivatives C⋮C → CH:C·COOR
s. *6*, 710; s. a. Soc. *1955*, 3636

Nickel carbonyl/triphenylphosphite $Ni(CO)_4/(C_6H_5)_3P$

Synthesis of trienes ←
s. *8*, 749

Via intermediates *v.i.*

Cyanoethylation of ketones via enamines H → CH_2CH_2CN
s. *9*, 912

Rearrangement

Hydrogen/Oxygen Type CC↓∩HO

Formic acid *HCOOH*

α,β-Ethyleneketones from α,β-acetylenealcohols ←
Rupe rearrangement
s. *5*, 508; s. a. R. Heilmann and R. Glenat, Bl. *1954*, 59

Hydrogen/Carbon Type CC↓∩HC

Without additional reagents *w.a.r.*

High pressure thermal reactions of hydrocarbons ←

$$C_6H_5CH(CH_3)_2 \rightarrow C_6H_5CH_2CH_2CH_3$$

Isopropylbenzene passed at 479° and 816 atm. through a stainless steel tube lined with copper and filled with copper pellets → n-propylbenzene. Y: 55.9% based on startg. m. consumed. Startg. m. reacted: 22.6%.—The reaction is non-catalytic. F. e. s. V. N. Ipatieff et al., Am. Soc. *75*, 3323 (1953).

trans-cis-Rearrangement ←
s. *8*, 750

β,γ-Ethylenenitriles from α,β-ethylene-α-cyanocarboxylic acids ←
s. *7*, 796

Aromatization ←
s. *6*, 711

by migration of a carbon-carbon double bond
Isomerization of cyclic sulfones
s. *9*, 779

Sodium hydroxide *NaOH*

cis-trans-Rearrangement ←

$$CH_3CH\overset{\text{trans}}{=\!=}CHCH\overset{\text{cis}}{=}CHCOOH \rightarrow CH_3CH\overset{\text{trans}}{=\!=}CHCH\overset{\text{trans}}{=\!=}CHCOOH$$

cis-trans-Sorbic acid refluxed 1.3 hrs. in 30%-NaOH → *trans-trans*-sorbic acid. Y: ca. 100%. U. Eisner, J. A. Elvidge, and R. P. Linstead, Soc. *1953*, 1372; alicyclics at room temp. s. C. Buchanan and A. C. Ritchie, Soc. *1954*, 4523.

Migration of carbon-carbon double bonds ←
Prototropic change s. *6*, 712

α,β- from β,γ-Ethyleneketones
s. *8*, 65

Potassium hydroxide *KOH*

Epimerization of steroids ←
s. *9*, 780

Migration of carbon-carbon double bonds ←
s. *8*, 751; with aniline s. 4, 259; with ethylene glycol s. T. R. Govindachari and B. R. Pai, J. Org. Chem. *18*, 1253 (1953)

Potassium hydroxide/alcohol

Migration of carbon-carbon triple bonds ←
s. *7*, 732

Sodium/alcohol *NaOR*

Migration of carbon-carbon double bonds ←
s. *9*, 781

α,β- from β,γ-Ethyleneketones
s. *9*, 87

Isomerization of cyclic β-ketocarboxylic acid esters ←
s. *3*, 591; s. a. J. O. Jilek, V. Šimák, and M. Protiva, Coll. Czech. Chem. Communs. *19*, 333 (1954); 2-stage procedure cf. N. N. Saha and P. Bagchi, J. Org. Chem. *20*, 1392 (1955)

Heterocyclics by internal Michael addition ○
s. *6*, 713

Nitrocyclopropane ring opening C
s. *6*, 225

Potassium/alcohol *KOR*

Migration of carbon-carbon double bonds ←
s. *7*, 733

Sodium amide $NaNH_2$

Alkylation of nitriles ←
with migration of carbon-carbon double bonds
s. *7*, 831

Potassium carbonate K_2CO_3

α,β-Acetylenecarboxylic acids ←
from β,γ-acetylenecarboxylic acids via α-allenecarboxylic acids

548. $HC{\equiv}C{\cdot}CH_2COOH \rightarrow H_2C{=}C{=}CHCOOH \rightarrow CH_3C{\equiv}C{\cdot}COOH$

3-Butynoic acid treated 3 hrs. at 40° with 18%-K-carbonate soln. → 2,3-butadienoic acid (Y: 92%) treated 6-8 hrs. at 90° with 18%-K-carbonate soln. → 2-butynoic acid (Y: 60%). E. Eglinton et al., Soc. *1954*, 3197.

Pyridine C_5H_5N

Aromatization by migration of carbon-carbon double bonds ←
s. *9*, 779

Cuprous chloride/copper *CuCl/Cu*

Cyclopentenones from divinylacetylenes ○
s. *7*, 734

Cuprous bromide *CuBr*

Allenes from acetylene derivatives ←
s. *9*, 782

Aluminum oxide *Al_2O_3*
s. *9*, 783

Aluminum alkoxide *$Al(OR)_3$*

cis-trans-Rearrangement ←
s. *7*, 735

Boron fluoride *BF_3*

α,β- from β,γ-Ethyleneketones ←
Steroids s. *9*, 784

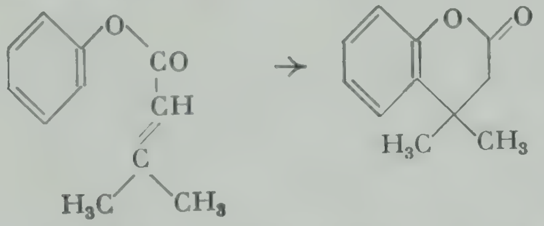
Boron fluoride/sulfuric acid *BF_3/H_2SO_4*

Cycloisomerization ○
s. *6*, 714

Aluminum chloride *$AlCl_3$*

Migration of carbon-carbon double bonds ←
s. *6*, 690

Cycloisomerization ○
3,4-Dihydro-coumarins and -carbostyrils



A mixture of phenyl β,β-dimethylacrylate, $AlCl_3$, and CS_2 stirred 3 hrs. at 35-47° → 4,4-dimethyl-3,4-dihydrocoumarin. Y: 67.5%.—In other cases, Fries rearrangement takes place and chromanones or hydroxyindanones are obtained. F. e. s. J. Colonge and R. Chambard, Bl. *1953*, 573; 3,4-dihydrocarbostyrils, also carbostyrils with elimination of phenyl s. Bl. *1953*, 982.

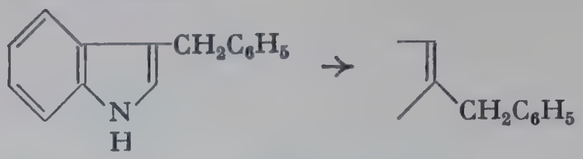
Ring expansion of isocyclics ←
s. *8*, 752

Aluminum chloride/sodium chloride *$AlCl_3/NaCl$*

Alkyl migration – Baddeley rearrangement ←
s. *9*, 940; without NaCl cf. D. E. Pearson and J. D. Bruton, J. Org. Chem. *19*, 957 (1954)

Position shift of side chains

549a.



N-heterocyclics. 1 g. 3-benzylindole heated 20 min. at 240° with AlCl
NaCl (10:1) → 0.63 g. 2-benzylindole. G. R. Clemo and J. C. Seato
Soc. *1954*, 2582.

Cycloisomerization
s. *8*, 893; *9*, 785

Aluminum chloride/hydrochloric acid *AlCl$_3$/H*

Alkyl migration ←
s. *6*, 833

Aluminum bromide *AlBr*

Isomerization of saturated hydrocarbons ←
s. *8*, 753

Buffer pH 7.8 ←

Rearrangement of N-condensed heterocyclics ←
s. *9*, 786

Formic acid/sulfuric acid s. Sulfuric acid/formic acid *HCOOH/H$_2$SO*

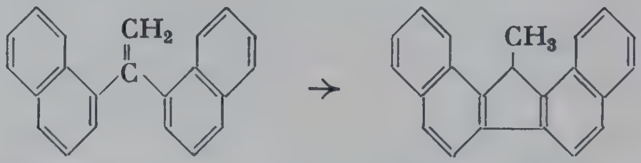
Acetic acid *CH$_3$COO*

cis- from trans-Condensed rings ←
s. *9*, 787

Stannic chloride *SnCl*

Cycloisomerization

550.



9-Alkyldibenzofluorenes. 1 g. 1,1-(di-1-naphthyl)ethylene thoroughl
mixed with anhydrous SnCl$_4$, stirred 2 min. at room temp., then de
composed with dil. HCl → 0.82 g. 9-methyl-1,2,7,8-dibenzofluorene. F
e. s. G. Wolf, Am. Soc. *75*, 2673 (1953).

Hydrazine/sodium/alcohol *H$_2$N·NH$_2$/NaO*

Migration of carbon-carbon double bonds ←
s. *6*, 117

Nitric acid *HNO*

Epimerization of sec. carboxyl groups ←
s. *8*, 754

Phosphorus pentoxide *P$_2$O*

Isotopic position isomerization ←
s. *9*, 788

Phosphoric acid *H_3PO_4*

Cycloisomerization ○

s. *8*, 755

Sulfur dioxide *SO_2*

Migration of double bonds ←

s. *9*, 789

p-Toluenesulfonic acid *TsOH*

cis-trans-Rearrangement ←

s. *6*, 715

Sulfuric acid *H_2SO_4*

s. *7*, 736

Migration of carbon-carbon double bonds ←

s. *6*, 716

to conjugated double bonds

s. *6*, 717; s. a. R. Howe and F. J. McGuillin, Soc. *1955*, 2423

5-Methyl-2(3H)-thiazolethiones from 5-methylene-2-thiazolidinethiones ←

s. *6*, 617

Sulfuric acid/formic acid *$H_2SO_4/HCOOH$*

Cycloisomerization with simultaneous hydration ○

Stereospecific reactions s. *9*, 790

Sulfuric acid/acetic acid *H_2SO_4/CH_3COOH*

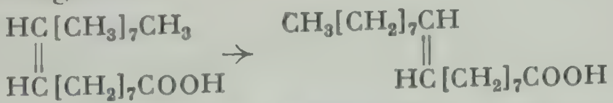
Dehydration-rearrangement ←

s. *7*, 888

Selenium *Se*

cis-trans-Rearrangement ←

1.



$$\begin{array}{c}\mathrm{HC[CH_3]_7CH_3}\\ \|\\ \mathrm{HC[CH_2]_7COOH}\end{array} \rightarrow \begin{array}{c}\mathrm{CH_3[CH_2]_7CH}\\ \|\\ \mathrm{HC[CH_2]_7COOH}\end{array}$$

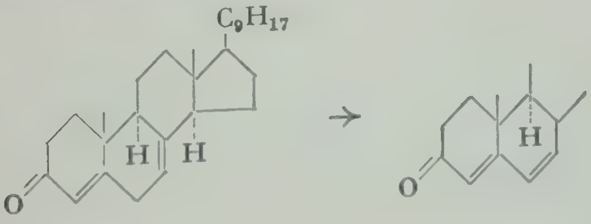
Oleic acid heated 1 hr. with Se at 220-225° in an atmosphere of CO_2 or N_2 → elaidic acid. Y: 62-64% based on the equilibrium mixture containing 67% elaidic acid. D. Swern and J. T. Scanlan, Biochem. Prep. *3*, 118 (1953); s. a. W. F. Huber, Am. Soc. *73*, 2730 (1951).

Hydrochloric acid *HCl*

s. *8*, 757

Migration of carbon-carbon double bonds to form conjugated double bonds ←

2.



16 g. crude ergosterone in dry chloroform treated with a stream o
HCl at 0° for 1 hr. → 14.5 g. crude isoergosterone (startg. m. f.
F. Johnson, G. T. Newbold, and F. S. Spring, Soc. *1954*, 1302; s.
A. Shepherd et al., Am. Soc. *77*, 1212 (1955).

s. a. *8*, 756

***α,β*- from *β,γ*-Ethyleneketones**
s. *8*, 65

Ketones from enolethers
with migration of a carbon-carbon double bond
s. *9*, 86

Migration of carbon-carbon double bonds and acetylation
Steroids s. *9*, 791

Naphthalene from indole ring
by migration of carbon-carbon double bonds,
with simultaneous esterification
s. *9*, 792

Ethylene derivatives from cyclopropane ring
Isosteroids s. *7*, 737

Chlorides from ethylene derivatives with rearrangement
s. *6*, 554

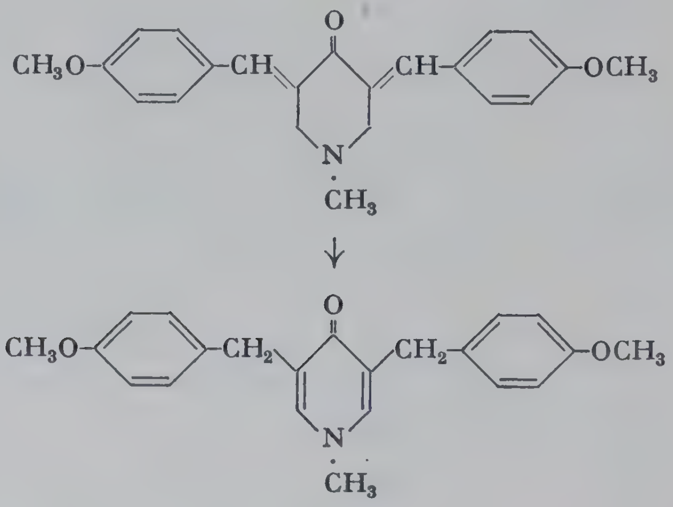
Palladium-carbon *F*

Epimerization
s. *6*, 838

Palladium-carbon/ethylene glycol

4-Pyridones from 4-piperidones

553.



A mixture of 1-methyl-3,5-di-(p-methoxybenzylidene)-4-piperidone
Pd-on-carbon in ethylene glycol refluxed 0.5 hr. → 1-methyl-3,5-di
methoxybenzyl)-4-pyridone. Y: 85%. F. e. s. N. J. Leonard and D.
Locke, Am. Soc. *77*, 1852 (1955).

Via intermediates *v.i.*

Migration of carbon-carbon double bonds via dihydrospiro-1,3-oxazines ←
s. *8*, 413

Inversion of configuration – Stereospecificity ←
s. *7*, 738

trans- from cis-Condensed rings via enolates ←
s. *8*, 758

Oxygen/Carbon Type CC↶OC

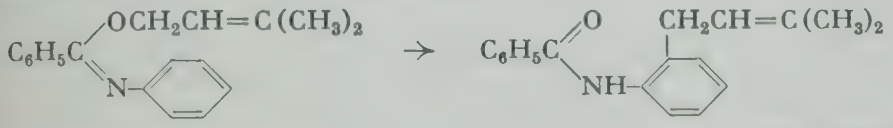
Without additional reagents *w.a.r.*

Claisen rearrangement ←
s. *7*, 739

Allylphenols from allyl ethers
s. *2*, 621; *4*, 671; s. a. A. B. Sen and R. P. Rastogi, J. Indian Chem. Soc. *30*, 355 (1953)

Carboxylic acid amides from iminoesters ←

54.



N-Phenylbenzimidoyl γ,γ-dimethylallyl ether heated to 255-260°, heating discontinued until the exothermic reaction subsides, then kept at 220-225° for a total of 2 hrs. → o-benzamido-γ,γ-dimethylallylbenzene. Y: 75%. W. M. Lauer and R. G. Lockwood, Am. Soc. *76*, 3974 (1954).

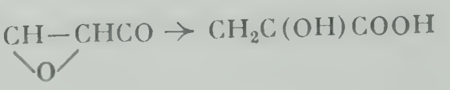
Lithium *Li*

Phenanthrene ring from O-heterocyclics ←
Intraanionic isomerization
Ring contraction s. *8*, 759

Sodium hydroxide *NaOH*

Aromatization by enolization ←
s. *8*, 760

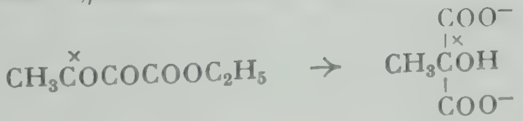
α-Hydroxycarboxylic acids from α,β-oxidoketones
s. *6*, 901



$$\underbrace{CH{-}CH}_{O}CO \rightarrow CH_2C(OH)COOH$$

Tartronic acids from α,β-diketocarboxylic acid esters ←

'5.



$$CH_3\overset{\times}{C}OCOCOOC_2H_5 \rightarrow CH_3\overset{\times}{C}(COO^-)_2OH$$

An aq. soln. of ethyl α,β-diketobutyrate-β-C^{14} added to cooled aq. NaOH, the ice bath removed after a few min., the soln. allowed to stand for 2 days, and the product isolated as the Ba-salt → Ba-methyltartronate-α-C^{14}. Y: 97.5%. H. W. Davis, E. Grovenstein, Jr., and O Neville, Am. Soc. *75*, 3304 (1953).

Indenones from hydroxynaphthoquinones
s. *7*, 740

Naphthalenes from 4,5-benzotropolones
s. *7*, 741

Potassium hydroxide *K*

Spiroindoxyls from carbazole ring
s. *7*, 742

Potassium hydroxide/pyridine *KOH/*C_5

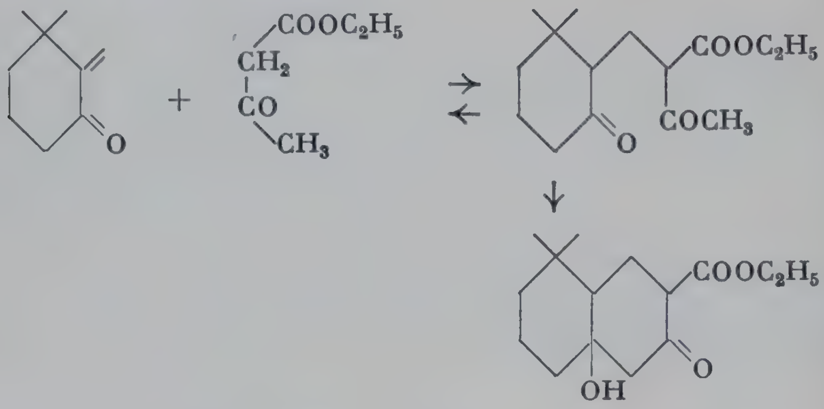
Baker-Venkataraman transformation
s. *6*, 868

Sodium/alcohol *Na*

Claisen rearrangement
Transetherification with simultaneous transesterification
Deformylation
s. *7*, 743

Ring closure by aldol condensation

556.



A mixture of 0.5 g. diketoester (centre formula), ethyl acetoacet and Na-ethoxide allowed to stand 2 hrs. at room temp. → 0.28 g. cyclic hydroxyketoester.—The presence of ethyl acetoacetate serve shift the equilibrium. No ring closure takes place in its absence. Stauffacher and H. Schinz, Helv. *37*, 1227 (1954).

Ethylenealcohols from cyclic ethers
s. *7*, 744

Pyrrolidiones from oxazolidones
s. *7*, 745

Ethyl sodioacetoacetate/pyridine

Baker-Venkataraman transformation
s. *6*, 868

Phenyllithium and potassium amide *C_6H_5Li and KNH_2*

Wittig rearrangement – Alcohols from ethers ←
s. *7*, 746

Cupric sulfate *$CuSO_4$*

Rearrangement of acoxyethylenes ←
s. *7*, 747

Zinc acetate *$(CH_3COO)_2Zn$*

Indoles from aminochromes ←
s. *7*, 514

Zinc chloride/acetic anhydride *$ZnCl_2/(CH_3CO)_2O$*
s. Acetic anhydride/zinc chloride

Alumina *Al_2O_3*

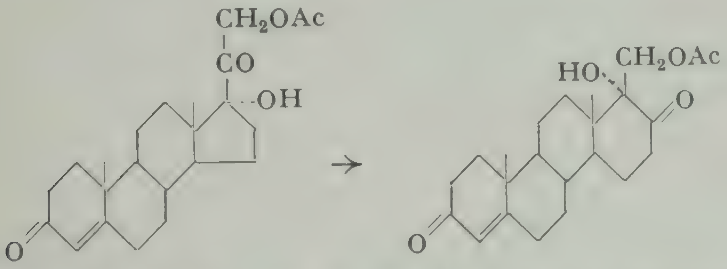
Pinacol rearrangement ←
s. *8*, 761

β-Diketones from enolesters ←
s. *8*, 762

Aluminum alkoxide *$Al(OR)_3$*

D-Homo rearrangement of steroids ←

7.



Ring expansion. A soln. of 17α-hydroxydesoxycorticosterone 21-acetate and Al-isopropoxide in dry toluene refluxed 1 hr. with cyclohexanone → 17aβ-acetoxymethyl-D-homo-Δ^4-androsten-17aα-ol-3,17-dione. Y: 46%.
E. Batres, G. Rosenkranz, and F. Sondheimer, Am. Soc. *76*, 5171 (1954).

Boron fluoride *BF_3*

Fries rearrangement ←
s. *7*, 748; *10*, 589

Aldehydes from oxido compounds ←
s. *9*, 793; s. a. Am. Soc. *77*, 3071 (1955)

ψ-Oxindoles from ψ-indoxyls ←
s. *9*, 794

Aluminum chloride *$AlCl_3$*

Phenolketones from phenolesters ←
Unusual Fries rearrangement
s. *6*, 718

Cyclic ketocarboxylic acids from carboxylic acid anhydrides ←
in CS_2 s. *8*, 903; in nitrobenzene s. A. D. Campbell, Soc. *1954*, 3659

Furostenes from spirostanes ↺
s. *9*, 795

Acetic anhydride *$(CH_3CO)_2O$*

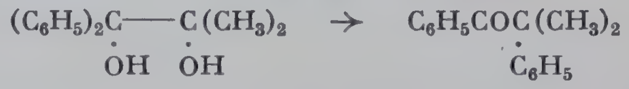
Enolesters from enolethers with rearrangement ←
s. *7*, 313

Furostenes from spirostanes ↺
s. *7*, 749; s. a. M. E. Wall, H. E. Kenney, and E. S. Rothman, Am. Soc. *77*, 5665 (1955)

Acetic anhydride/zinc chloride *$(CH_3CO)_2O/ZnCl_2$*

Ketones from glycols with C-rearrangement ←

558.



$$(C_6H_5)_2\underset{OH}{\dot{C}}-\underset{OH}{\dot{C}}(CH_3)_2 \rightarrow C_6H_5CO\underset{C_6H_5}{\dot{C}}(CH_3)_2$$

Acetic anhydride added to a mixture of 2-methyl-1,1-diphenylpropane-1,2-diol and fused, pulverized $ZnCl_2$, heated 5 min. on a steam bath, and allowed to stand 1 hr. at room temp. → α-phenylisobutyrophenone. Y: 85%. R. E. and G. G. Lyle, J. Org. Chem. *18*, 1058 (1953).

Formic acid *HCOOH*

Aldehydes and ketones from glycol monoethers ←
s. *7*, 750

α-Acoxyketones from p-dioxanes ↺
s. *9*, 796

Acetyl chloride *CH_3COCl*

Pinacol rearrangement ←
with subsequent hydrolytic cleavage of the carbon chain
s. *9*, 797

Polyphosphoric acid *$H(PO_3H)_xOH$*

Cyclic ketocarboxylic acids ←
from dicarboxylic acid anhydrides
s. *10*, 559

Thionyl chloride *$SOCl_2$*

Ethylenecarboxylic acid esters from lactones ↺
s. *8*, 763

p-Toluenesulfonic acid *TsOH*

Dienone-phenol rearrangement ←
s. *7*, 751

Sulfuric acid *H_2SO_4*

Phenol acetates from dienones ←
Ring expansion s. *6*, 720

Pinacol rearrangement ←
s. *6*, 719; ring expansion s. *7*, 753

Steroids from 3,5-cyclosteroids C
s. *9*, 798

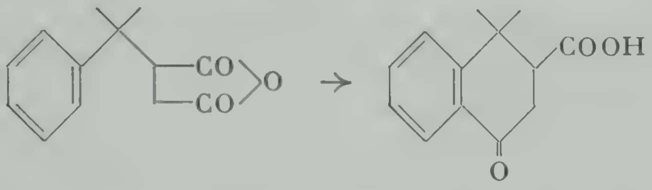
Ring opening of O-heterocyclics
s. *7*, 752

Hydroxyenolethers from inner acetals
s. *9*, 799

Cyclobutanes from cyclopropanes ←
s. *6*, 721

Cyclic ketocarboxylic acids from dicarboxylic acid anhydrides ←

9.



37.2 g. α,α-dimethylbenzylsuccinic anhydride dissolved in concd. H_2SO_4, then heated 2 hrs. on a steam bath → 26.5 g. 4,4-dimethyl-3-carboxy-1-tetralone.—The formation of a 6-membered ring is preferred to the exclusion of the 5-membered alternative. F. e. s. R. S. Urban and E. M. Beavers, Am. Soc. *76*, 3042 (1954); with polyphosphoric acid s. H. A. Lloyd and E. C. Horning, Am. Soc. *76*, 3651 (1954).

O-Heterocyclics from ketones by rearrangement ←
s. *8*, 764

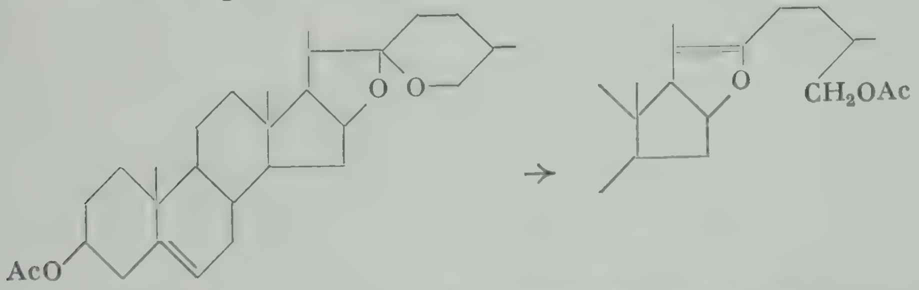
Iodine/acetic acid *I/CH_3COOH*

Ring expansion by pinacol rearrangement ←
s. *7*, 753

Pyridine hydrochloride *C_5H_5N,HCl*

Furostenes from spirostanes C

).



A mixture of 22-iso-5-spirosten-3β-ol acetate, acetic anhydride, and dry pyridine hydrochloride refluxed 5 hrs. → furosta-5,20(22)-diene-3β,26-diol diacetate. Y: 84%. W. G. Dauben and G. J. Fonken, Am. Soc. *76*, 4618 (1954).

Hydrochloric acid *HCl*

1,5-Anionotropic rearrangement ←
s. *8*, 765

Ethers from diols
s. *7*, 754

Dienone-phenol rearrangement ←
s. *8*, 766

Hydrobromic acid *HBr*

Aromatization by enolization ←
Ethers s. *9*, 800

Nitrogen/Nitrogen Type CC↶NN

Without additional reagents *w.a.r.*

Thiazoles from thiosemicarbazides with benzidine rearrangement ←
s. *6*, 646

Phthalic anhydride ←

Benzidine type rearrangement ←
s. *8*, 767

Nitrogen/Carbon Type CC↶NC

Without additional reagents *w.a.r.*

Ethyleneacylamines from dihydrospiro-1,3-oxazines C
s. *8*, 413

Sodium hydroxide *NaOH*

Hofmann degradation of quaternary ammonium salts
Ring opening of N-heterocyclics

Ethylene derivatives from amines
s. *6*, 722

Ring opening via quaternary ammonium salts
s. *8*, 768

Quinoline from isatin ring ←
s. *6*, 723

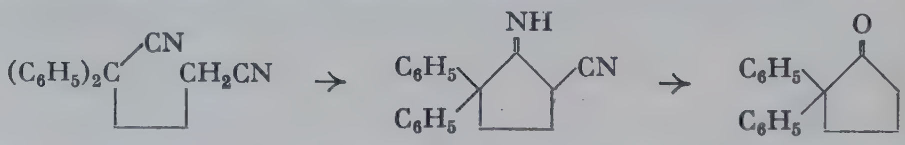
Potassium hydroxide *KOH*

Hofmann degradation of quaternary ammonium salts
Ring opening of N-heterocyclics C
s. *6*, 724

Sodium/alcohol *NaOR*

Cyclic ketones from dinitriles via cyclic β-iminonitriles ○

561.



2,2-Diphenyladiponitrile dissolved in a soln. of Na in dry *tert*-butanol with heating and swirling, then refluxed 3.5 hrs. → crude 5-cyano-2,2-

diphenylcyclopentanoneimine (Y: ca. 100%), finely powdered, added slowly with stirring to H_2SO_4-water, heated on a steam-bath until dissolved, then for 15 min. more → 2,2-diphenylcyclopentanone (startg. m. f. 425). Y: 81%. N. R. Easton and S. J. Nelson, Am. Soc. *75*, 640 (1953).

Phenyllitium C_6H_5Li

Tert. amines from quaternary ammonium salts by rearrangement via ylides ←

s. *7*, 755

Lithium methylanilide $(C_6H_5)(CH_3)N{\cdot}Li$

Ziegler ring closure of dinitriles ○

s. *5*, 525; cyanoketones as products s. C. W. Muth, D. O. Steiniger, and Z. B. Papanastassiou, Am. Soc. *77*, 1006 (1955)

Sodium amide $NaNH_2$

o-Substitution rearrangement of quaternary ammonium salts ←

s. *8*, 769

Zinc *Zn*

Nitriles from formamides via isonitriles NHCHO → CN

s. *9*, 801

Lithium aluminum hydride $LiAlH_4$

Amines from carboxylic acid amides with rearrangement ←

s. *8*, 770

Aluminum chloride $AlCl_3$

Phenanthridones from isocyanates ○

s. *5*, 526; s. a. W. L. Mosby, Am. Soc. *76*, 936 (1954)

Acetic anhydride/sodium hydroxide $(CH_3CO)_2O/NaOH$

Racemization of α-aminocarboxylic acids ←

Selective O-deacetylation

s. *8*, 771

Polyphosphoric acid $H(PO_3H)_xOH$

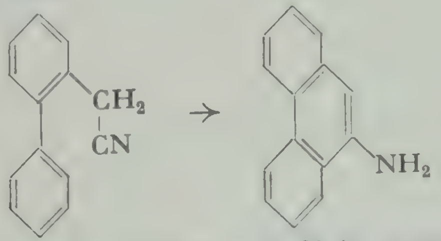
Lactams from isocyanates ○

s. *10*, 665

Sulfuric acid H_2SO_4

Ar. amines from nitriles ○

62.



2-Biphenylylacetonitrile kept 3 hrs. at 0° in concd. H_2SO_4 → 9-phenanthrylamine. Y: 85%. F. e. s. C. K. Bradsher, D. J. Beavers, and E. D. Little, Am. Soc. *76*, 948 (1954).

Hydrochloric acid *HCl*

1,2,3,4-Tetrahydroisoquinolines from azomethines
s. *6*, 725

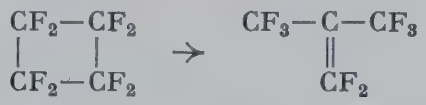
Enamines from cyclic imines C
s. *7*, 756

Halogen/Carbon Type CC↓∩HalC

Without additional reagents *w.a.r.*

Ring opening by isomerization C

563.



$$\begin{array}{c} CF_2-CF_2 \\ | \quad\quad | \\ CF_2-CF_2 \end{array} \rightarrow \begin{array}{c} CF_3-C-CF_3 \\ \| \\ CF_2 \end{array}$$

Perfluorocyclobutane passed at 720° through a carbon-lined tube → perfluoroisobutene (startg. m. f. 420). Y: 70%. T. J. Brice et al., Am. Soc. *75*, 2698 (1953).

Cuprous chloride *CuCl*

Rearrangement of ethylenehalides ←
s. *8*, 772

1,3-Dienes from allenes
s. *8*, 773

Sulfur/Carbon Type CC↓∩SC

Without additional reagents *w.a.r.*

10-Alkylidenethiaxanthenes from 10-alkylthiaxanthylium salts ←
s. *8*, 774

Sodium/alcohol *NaOR*

Thioethers from sulfonium salts with rearrangement ←
s. *6*, 726

Alkali amide ←

Mercaptans from thioethers ←
and thioethers from sulfonium salts with o-rearrangement
s. *8*, 775

Carbon/Carbon Type CC↓∩CC

Without additional reagents *w.a.r.*

Rearrangement of carbon-carbon bonds ←
s. *8*, 776

Sodium alkoxide *NaOR*

Carboxylic acid esters from α-halogenoketones ←
Favorskiĭ rearrangement
s. *8*, 777

Sodium nitrite *$NaNO_2$*

Cyclic ketones from 2-aminoalcohols by ring expansion ←
s. *1*, 541; s. a. F. Ramirez and S. Stafiej, Am. Soc. *77*, 134 (1955)

Sulfuric acid *H_2SO_4*

Anthrones from indanones ←
s. *7*, 757

Exchange

Hydrogen ↑ CC⇅H

Without additional reagents *w.a.r.*

Cyanogenation H → CN
s. *9*, 802

Irradiation ←

Dimerization ←
s. *8*, 948

Sodium *Na*

2-Subst. quinolines via 2-subst. 1,2-dihydroquinolines ←
s. *8*, 778

Potassium hydroxide/oxygen s. Oxygen/potassium hydroxide *KOH/O_2*

Phenyllithium *C_6H_5Li*

Carboxylic acid esters from hydrocarbons H → COOR
Synthesis with addition of 1 C-atom
s. *9*, 803

Potassium amide *KNH_2*

Indole ring ○
s. *7*, 758

Triethylamine *$(C_2H_5)_3N$*

Quinolyl-α-cyanocarboxylic acid esters RCH(CN)COOR
s. *7*, 759

Mercuric fulminate *$Hg(ONC)_2$*

Cyanogenation H → CN
s. *6*, 727

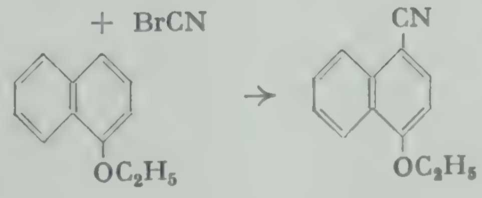
Zinc chloride *$ZnCl_2$*

Introduction of aldehyde groups into ar. rings H → CHO
Gattermann synthesis
s. *7*, 760

Aluminum chloride *$AlCl_3$*

Cyanogenation H → CN

4.



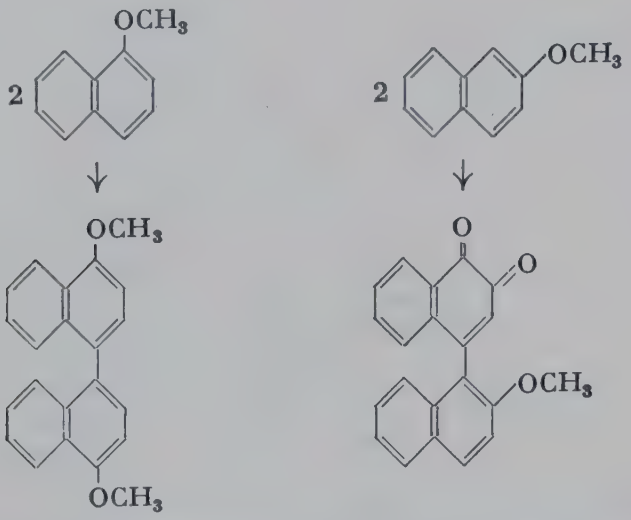
1-Ethoxynaphthalene allowed to react with cyanogen bromide in CS_2 containing $AlCl_3$ → 4-ethoxy-1-naphthonitrile. Y: 80%. F. e. s. G. W. Gray and B. Jones, Soc. *1954*, 678; method s. P. Karrer, A. Rebmann, and E. Zeller, Helv. *3*, 267 (1920).

Ar. nitro compounds *$ArNO_2$*

Oxidative dimerization 2 RH → R·R
s. *7*, 761

Performic acid *$HCOO_2H$*

565.



A mixture of 30%-H_2O_2 and formic acid added dropwise at 40° during 90 min. with stirring to a soln. of α-naphthyl methyl ether, stirring continued for 15 min., then allowed to stand 12 hrs. at room temp. → 4,4′-dimethoxy-1,1′-dinaphthyl. Y: 70%.—Similarly: Nerolin → 4-(2-methoxy-1-naphthyl)-1,2-naphthoquinone. Y: 64.3%. H. Fernholz and G. Piazolo, B. *87*, 578 (1954).

Chloranil ←

Benzene ring synthesis – Condensed isocyclics ○
s. *6*, 728

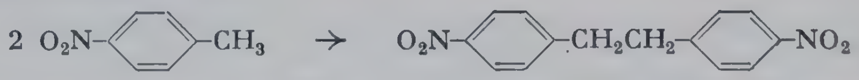
Oxygen *O_2*

Oxidative condensation ←
s. *8*, 779

Oxygen/potassium hydroxide *O_2/KOH*

Oxidative dimerization 2 RH → R·R

566.



p-Nitrotoluene added at 10° to methanolic 30%-KOH, then a rapid stream of air passed through with vigorous stirring for 3 hrs., the ice bath removed, and the passage of air continued for an additional 5 hrs. → p,p′-dinitrobibenzyl. Y: 74-76%. H. O. House, Org. Synth. *34*, 35 (1954).

Sulfur *S*

Ethylene derivatives by dimerization $2\,RCH_3 \rightarrow RCH{:}CHR$

s. *9*, 804

Persulfate $S_2O_8^{--}$

Oxidative dimerization of aliphatic nitro compounds $2\,RH \rightarrow R\cdot R$

s. *9*, 805

Bromine *Br*

Dienes from ethylene derivatives by dimerization $2\,RH \rightarrow R\cdot R$

s. *8*, 780

3-Halogenoquinolines ○

s. *7*, 762

Palladium/oxygen Pd/O_2

Oxidative dimerization $2\,RH \rightarrow R\cdot R$

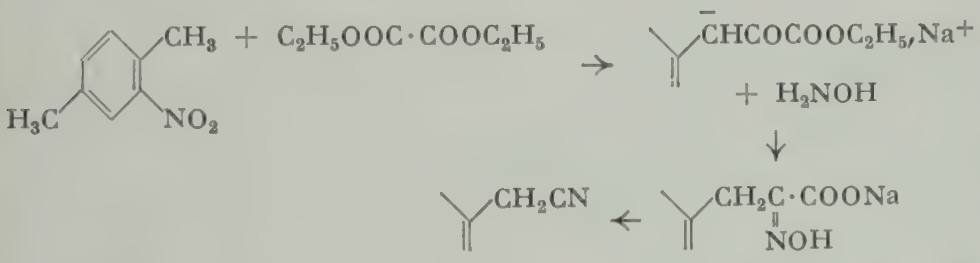
s. *7*, 763

Via intermediates *v.i.*

α,β-Ethylenenitriles from ethylene derivatives H → CN

s. *9*, 899

Cyanogenation via α-ketocarboxylic acid ester Na-enolates and α-oximinocarboxylic acids



Abs. ether, nitro-p-xylene, and diethyl oxalate added to ethanol-free Na-ethoxide (prepn. s. original), and refluxed 42 hrs. with stirring → crude ethyl 2-nitro-4-methylphenylpyruvate Na-enolate (Y: 80.7%) dissolved in water, heated 1 hr. on a steam bath, filtered, NaCl followed by an aq. soln. of hydroxylamine hydrochloride and NaOH added, allowed to stand 1 hr. at room temp., then overnight at 8° → crude Na-2-nitro-4-methylphenylpyruvate oxime (Y: 70.2%), 281 g. added in small portions at 70° to a mixture of glacial acetic acid and acetic anhydride, dil. with cold water, and kept at 8° overnight → 195 g. 2-nitro-4-methylphenylacetonitrile. H. R. Snyder and J. K. Williams, Am. Soc. *76*, 1298 (1954).

Oxygen ↓ CC⇅O

Without additional reagents *w.a.r.*

Methylene bridge with formaldehyde $2\,RH \rightarrow R\cdot CH_2\cdot R$

s. *9*, 806

Chloromethylation $H \rightarrow CH_2Cl$
s. *8*, 824; s. a. M. W. Miller, R. W. Amidon, and P. O. Tawney, Am. Soc. *77*, 2845 (1955)

Mannich reaction – Aminomethylation $H \rightarrow CH_2NR_2$

Replacement of hydrogen by methyl via tert. amines
Hydrogenolysis of Mannich bases
s. *6*, 730

Replacement of hydrogen by methyl
via tert. amines, acoxy compounds, and halides
s. *6*, 731

Mannich reaction with acylaminomalonic esters
s. *6*, 732

Aminoalkylation $H \rightarrow CHRNHR'$
s. *6*, 733

Alkylidenebarbituric acids $CHO \rightarrow CH{:}\overset{|}{\underset{|}{C}}$
s. *7*, 764

Methine condensation $\cdot CH{:}$
s. *6*, 729

Aldimines from hydrocarbons $CH_2 \rightarrow CHCH{:}NH$
s. *6*, 734

Synthesis of aliphatic nitro compounds from hydroxy compounds ←
s. *8*, 781

Salts of aci-α,γ-dinitroglutaric acid esters from aldehydes and nitroacetic acid ester ←
s. *9*, 856

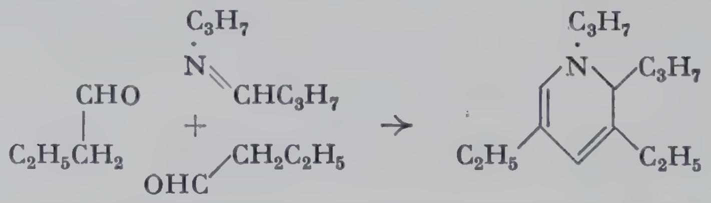
Lactones by phenol condensation ○
s. *7*, 765

Condensed 2-pyrone ring
s. *7*, 766

Piperidine ring synthesis – Guareschi reaction
s. *7*, 767

Dihydropyridines from aldimines and aldehydes
Azeotropic water separation

568.



A mixture of N-butylidenepropylamine and butyraldehyde brought to reflux, benzene added, and refluxing continued with azeotropic water separation until no more water is formed → 3,5-diethyl-1,2-dipropyldihydropyridine. Y: 66%.—This method offers a convenient route to many pyridine and piperidine derivatives not readily obtained by the conventional reaction of an aldehyde with an amine. F. e. s. T. M. Patrick, Jr., Am. Soc. *74*, 2984 (1952).

Pyridine ring

from enolether acetals	**from enamines**
s. *6*, 735	s. *9*, 807

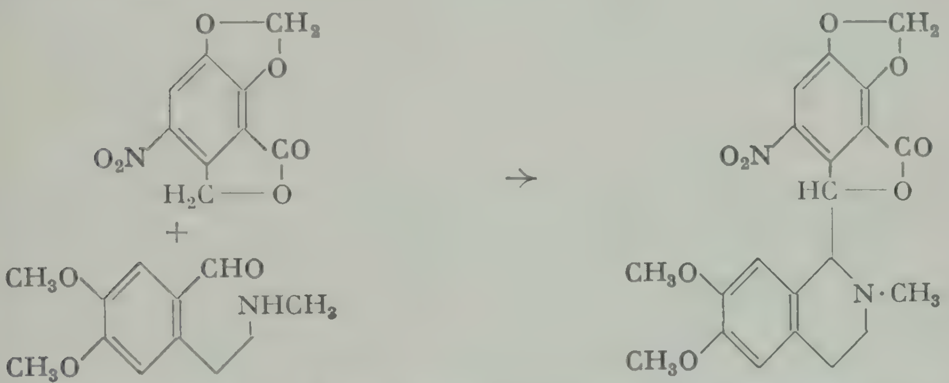
4-Piperidones

s. *9*, 808

Indoles from quinones – Nenitzescu indole ring synthesis

s. *8*, 782

1,2,3,4-Tetrahydroisoquinoline ring closure with side chain condensation



2.9 g. lodal and 1 g. 6.7-methylenedioxy-4-nitrophthalide refluxed 20 min. in alcohol → 1.63 g. (±)-nitrocorlumine. W. M. Whaley and M. Meadow, Soc. *1953*, 1067.

4-Hydroxyquinolines

s. *8*, 783

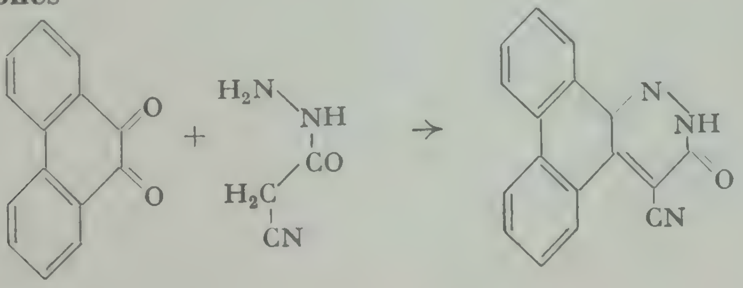
4-Hydroxycarbostyrils

s. *9*, 809; 1,3-dihydroxy-4,7-phenanthrolines s. A. L. Searles and R. M. Warren, J. Org. Chem. *18*, 1317 (1953); benzo[f]quinoline-1,3-diones s. F. F. Blicke and J. E. Gearien, Am. Soc. *76*, 3991 (1954)

N-Condensed heterocyclics

Quinolizones s. *8*, 784

6-Pyridazones



A suspension of 20.8 g. 9,10-phenanthrenequinone in anhydrous ethan refluxed 3 hrs. with 9.9 g. cyanoacetic acid hydrazide → 20 g. 3, (9′,10′-phenanthreno)-5-cyano-6-pyridazone. F. e. and methods s. I Schmidt and J. Druey, Helv. *37*, 134 (1954).

Pyrimidines from ureas via ureidomethylene compounds
s. *8*, 785; s. a. Am. Soc. *77*, 5867 (1955)

2,3,4,5-Tetrahydro-9(H)-pyrid[3,4-b]indoles
s. *8*, 786

Lithium *L*

Ketones

from carboxylic acids
s. *9*, 810; labeled compounds s. J. Meinwald, Am. Soc. *77*, 1617 (1955)

from carboxylic acid esters
s. *8*, 787

COOH ↘
COR
COOR ↗

Sodium *Na*

Ester condensation – Reactions with sodium dispersions ←

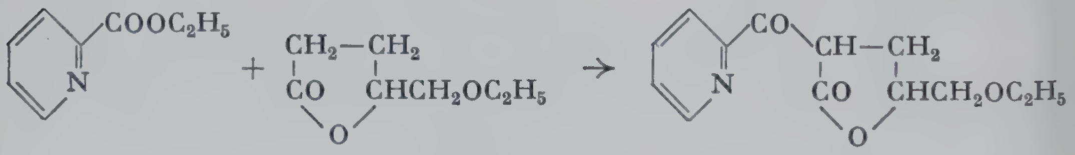
571. $2\ CH_3COOC_2H_5 \rightarrow CH_3COCH_2COOC_2H_5$

Na-dispersion (s. original) added with stirring to refluxing ethyl acetate, when the Na has dissolved after 15 min. the mixture transferred into a preheated autoclave, and heated 0.5 hr. under its own pressure at 100°/p. s. i. → ethyl acetoacetate. Y: ca. 100%. F. e. s. O. D. Frampton and J. F. Nobis, Ind. Eng. Chem. *45*, 404 (1953).

Potassium *K*

Synthesis of ketolactones COOR → COR′

572.



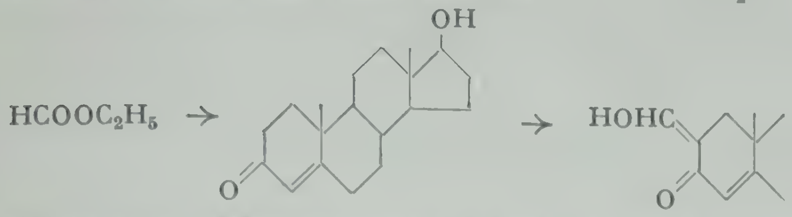
A mixture of δ-ethoxy-γ-valerolactone and ethyl 2-picolinate added to a suspension of K in benzene, kept 1 hr. at 20-30° with occasional cooling, then heated 1 hr. on a steam bath and allowed to stand overnight → 2-pyridyl α-(δ-ethoxy-γ-valerolactonyl)ketone. Y: 69%. K. Winterfeld and E. Müller, A. *581*, 77 (1953).

Sodium hydride *NaH*

Methylene bridge with formaldehyde $R{\cdot}CH_2{\cdot}R'$
s. *10*, 576

α-Hydroxymethyleneketones from ketones $CH_2 \rightarrow C{:}CHOH$

3.

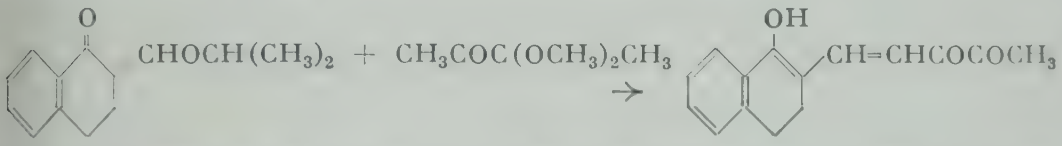


NaH added to a soln. of testosterone and ethyl formate in benzene, allowed to stand under N_2 for 3 days → hydroxymethylenetestosterone. Y: 83%. F. e. s. F. L. Weisenborn, D. C. Remy, and T. L. Jacobs, Am. Soc. *76*, 552 (1954).

β-Diketones $COCH_2CO$
s. *6*, 737

Condensation with alkoxymethylene compounds ←

4.

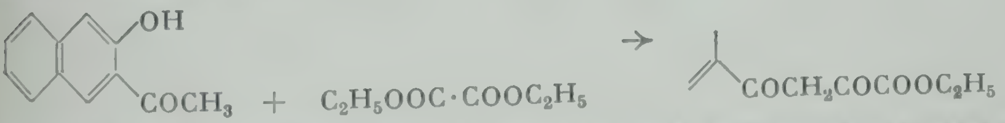


2-Isopropoxymethylenetetralone in dry tetrahydrofuran mixed at Dry Ice temp. under N_2 with a soln. of biacetyl monoketal and NaH in the same solvent, stirred 30 min. at 40° under N_2 → condensation product. Crude Y: 69%. F. e., with lower yield, s. E. Ott and D. S. Tarbell, Am. Soc. *74*, 6266 (1952).

α,β-Ethylenecarboxylic acid esters from ketones $CO \rightarrow C{:}CHCOOR$
s. *7*, 768

β-Ketocarboxylic acid esters
from carboxylic acid esters
Mixed ester condensation $COCH_2COOR$
s. *7*, 434; ball mill reactor s. *6*, 738

Oxalic ester synthesis $H \rightarrow COCOOR$
α,γ-Diketocarboxylic acid esters from ketones



2-Hydroxy-3-acetylnaphthalene allowed to react with ethyl oxalate and NaH with stirring and occasional ice-cooling, kept 2 hrs. at 0°, heated cautiously to 100°, heating then continued for 0.5 hr., and allowed to stand at 20° overnight → ethyl (3-hydroxy-2-naphthoyl)pyruvate. Y: 72%. F. e. s. H. Schmid and H. Seiler, Helv. *35*, 1990 (1952).

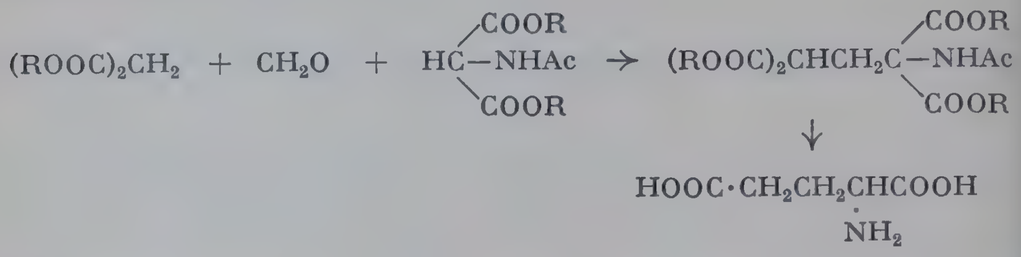
←

β-Ketoenollactones
s. *7*, 912

Sodium hydroxide *NaOH*

Methylene bridge with formaldehyde ←
α-Amino-γ-dicarboxylic acids

576.



$$(ROOC)_2CH_2 + CH_2O + HC\begin{smallmatrix}COOR\\-NHAc\\COOR\end{smallmatrix} \rightarrow (ROOC)_2CHCH_2C\begin{smallmatrix}COOR\\-NHAc\\COOR\end{smallmatrix} \rightarrow HOOC\cdot CH_2CH_2\underset{NH_2}{CH}COOH$$

Acetaminomalonic ester, 50% excess malonic ester, and 50% excess paraformaldehyde in xylene heated 5 hrs. at 100° in the presence of a catalytic amount of NaOH → methylene-malonic-acetaminomalonic ester (Y: ca. 80%) boiled 8 hrs. with concd. HCl → glutamic acid hydrochloride (Y: ca. 100%). Overall Y: 75%. H. Hellmann and F. Lingens, Ang. Ch. *66*, 201 (1954); first step with NaH s. H. *297*, 283 (1954).

Mannich reaction – Aminomethylation H → CH_2NR_2
Nitramines s. *6*, 739

α,β-Ethylenealdehydes from aldehydes ←
Dimerization s. *8*, 788

α,β-Ethyleneketones from aldehydes CHO → CH:CHCOR
Chalcones s. *6*, 740

4,5-Benzotropolones ○
s. *7*, 769

Subst. phthalides from o-aldehydocarboxylic acids
s. *9*, 811

2(1H)-Quinolylidene compounds
s. *8*, 789

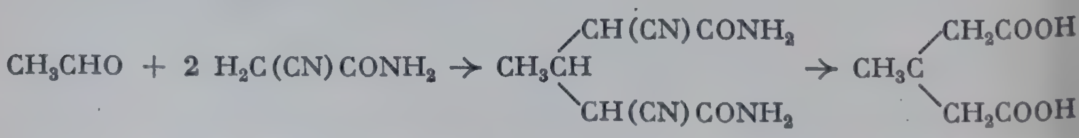
Potassium hydroxide *KOH*

Methylene bridge with formaldehyde 2 RH → $R\cdot CH_2\cdot R$
s. *1*, 547; sym. 1,5-diketones s. L. Mehr, E. I. Becker, and P. E. Spoerri, Am. Soc. *77*, 984 (1955)

α,β-Ethylenenitriles from aldehydes CHO → CH:C·CN
s. *7*, 271

β-Subst. glutaric acids from aldehydes ←
via α,α′-dicyanoglutaramides

577.



$$CH_3CHO + 2\ H_2C(CN)CONH_2 \rightarrow CH_3CH\begin{smallmatrix}CH(CN)CONH_2\\ \\CH(CN)CONH_2\end{smallmatrix} \rightarrow CH_3C\begin{smallmatrix}CH_2COOH\\ \\CH_2COOH\end{smallmatrix}$$

An aq. soln. of cyanoacetamide mixed with acetaldehyde and aq. 50%-KOH, the product collected after 3 hrs. → crude α,α′-dicyano-β-methylglutaramide (Y: ca. 95%) warmed with concd. HCl until dissolved, water added, and boiled 5 hrs. → β-methylglutaric acid (Y: ca. 100%). F. e. s. J. N. E. Day and J. F. Thorpe, Soc. *1920*, 1465; s. a. J. M. Osbond, J. D. Fulton, and D. F. Spooner, Soc. *1952*, 4785.

Aldol condensation with subsequent formation of azomethines ←

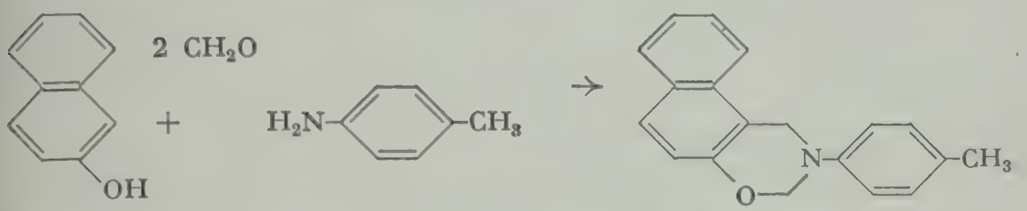
s. *6*, 741

Condensed cyclohexenolones ○

s. *9*, 812

2,3-Dihydro-1,3-öxazine ring synthesis

3.



Paraformaldehyde dissolved in hot methanol in the presence of a little KOH, the resulting soln. added slowly with cooling to a soln. of p-toluidine in methanol, then 2-naphthol in methanol added, and kept 2 days at 5° → 2,3-dihydro-2-p-tolyl-1H-naphth[1,2-e]-m-oxazine. Y: 91%. F. e. s. W. J. Burke, K. C. Murdock, and G. Ec, Am. Soc. *76*, 1677 (1954).

Alkali/alcohol ←

β-Ketocarboxylic acid esters from carboxylic acid esters

COCHRCOOR′

s. *7*, 771

Potassium hydroxide/alcohol ←

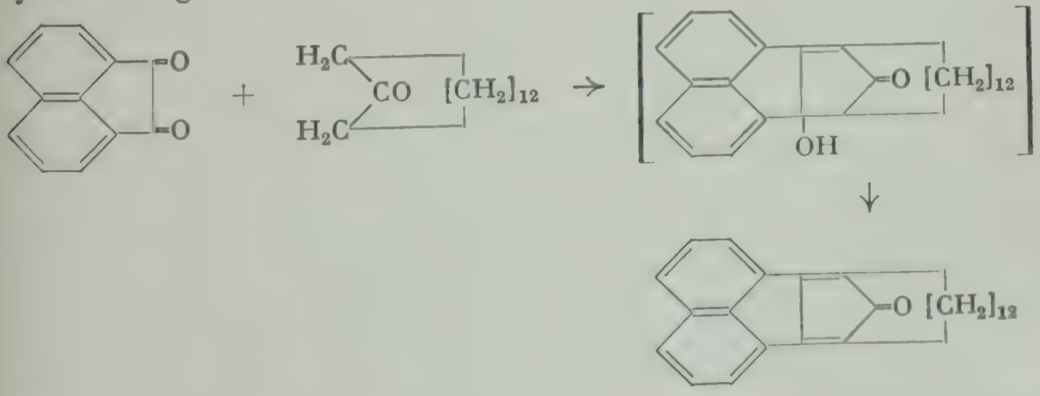
α,β-Ethyleneketones from aldehydes

CHO → CH:CHCOR

s. *8*, 790

Cyclone ring ○

1.



Macrocyclic ketones having over 13 ring members readily condense with benzil and acenaphthenequinone to give unsatd. macrocyclic compounds containing a CO-bridge and 2 double bonds, these groups forming a crossed conjugated system. These substances comprise a new class of carbonyl bridge compounds characterized by a double bond at each bridgehead.—E: A mixture of acenaphthenequinone, cyclopentadecanone, and methanolic KOH refluxed → 8-19-dodecahydro-7,20-methanocyclohexadeca[1,2-a]acenaphthylen-21-one (startg. m. f. 208). Y: 90%. F. e., also isolation of the intermediate, s. C. F. H. Allen and J. A. VanAllan, J. Org. Chem. *18*, 882 (1953).

Potassium hydroxide/acetic anhydride $KOH/(CH_3CO)_2O$

Cumulenes from acetylenealcohols ←

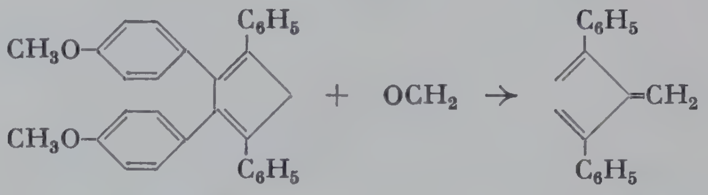
s. *7*, 770

Sodium/alcohol *NaOR*

Fulvenes

$CH_2 \rightarrow C{:}CH_2$

580.



A 4% soln. of Na in methanol added dropwise to a refluxing soln. of 2,5-diphenyl-3,4-bis-(4′-methoxyphenyl)cyclopenta-2,4-diene, 40%-formalin, and a 1:1 mixture of benzene and methanol, refluxing continued for 1 hr. → 1,4-diphenyl-2,3-bis-(4′-methoxyphenyl)fulvene. Y: 79%. D. Taber, E. I. Becker, and P. E. Spoerri, Am. Soc. *76*, 776 (1954); 6-subst. fulvenes s. Am. Soc. *77*, 1010 (1955).

α,β-Ethyleneketones from ketones ←

s. *6*, 742

Reactions of benzils with ketones ←

s. *8*, 791

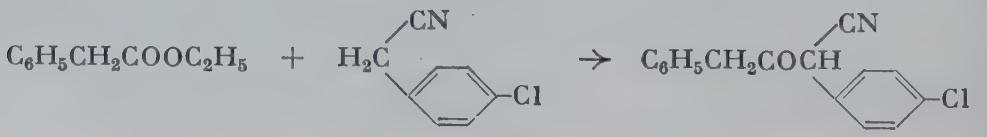
β-Diketones from carboxylic acid esters

COOR → COR′

s. *8*, 792

α-Cyanoketones from nitriles

581.



A mixture of 4-chlorophenylacetonitrile and ethyl phenylacetate added slowly to a soln. of Na in ethanol, and refluxed 3 hrs. → α-(4-chlorophenyl)-γ-phenylacetoacetonitrile. Y: 90%. F. e. s. S. B. Coan and E. I. Becker, Am. Soc. *76*, 501 (1954); Org. Synth. *35*, 30 (1955); s. a. G. A. Stein, H. A. Bronner, and K. Pfister, 3rd, Am. Soc. *77*, 700 (1955).

Malonic ester synthesis with free halogenocarboxylic acids

Hal → CH_2COOH

s. *8*, 793

Oxalic ester synthesis H → COCOOR
s. *10*, 567; with transesterification s. *10*, 209

α,γ-Diketocarboxylic acid esters from ketones
s. *10*, 162

Benzene ring synthesis ○
s. *6*, 743

4-Pyrones s. *9*, 813

Coumarin ring s. *9*, 814

Pyridine ring synthesis
s. *9*, 815

Thiophene ring s. *7*, 773

Thiophene 1,1-dioxides s. *6*, 744; *8*, 868

Sodium alkoxide

α-Keto-γ-lactones

from ketones s. *6*, 746

Simplified procedure s. *6*, 745

Sodium methoxide

α-Hydroxymethyleneketones from ketones $CH_2 \rightarrow C{:}CHOH$
s. *8*, 807

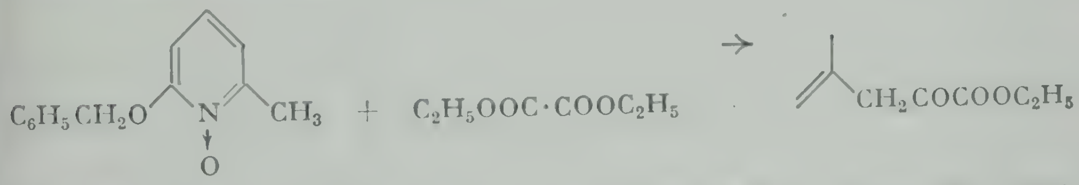
β-Ketoacetals from ketones via α-hydroxymethyleneketones $COCH_3 \rightarrow COCH_2CH(OR)_2$
s. *9*, 816; cf. Am. Soc. *77*, 3155 (1955)

Dienollactones s. *9*, 817

2,3-Pyrrolidiones s. *9*, 818 ○

Potassium/alcohol (Potassium alkoxide) *KOR*

Oxalic ester synthesis H → COCOOR



cf. Synth. Meth. *1*, 562; *2*, 646; s. a. A. Stoll et al., Helv. *38*, 1452 (1955). **N-Oxides as intermediates.** Active methyl groups of N-heterocyclics can be further activated by converting the compounds into the N-oxides.—E: 6-Benzyloxy-2-methylpyridine 1-oxide condensed with ethyl oxalate in the presence of K-ethoxide → ethyl 6-benzyloxy-2-pyridylpyruvate 1-oxide. Y: 64%. F. e., with lower yields, s. R. Adams and S. Miyano, Am. Soc. *76*, 3168 (1954).

Carboxylic acids from hydrocarbons via α-ketocarboxylic esters and acids
Synthesis with addition of 1 C-atom
s. *6*, 747

Polyenedicarboxylic acids via enolesters
s. *7*, 774

α,β-Ketodicarboxylic acid esters
s. *6*, 858

n-Butyllithium *n*-C_4H_9Li

Synthesis of sym. ketones with carbon dioxide $2\ RH + CO_2 \rightarrow R_2CO$
Metalation of thiophenes s. *9*, 819

Phenyllithium C_6H_5Li

Ethylene derivatives from ethers ←
Dimerization s. *7*, 746

Triphenylmethylsodium $(C_6H_5)_3C{\cdot}Na$

Oxalic ester synthesis $H \rightarrow COCOOR$
α-Keto-β-dicarboxylic acid esters from carboxylic acid esters
s. *7*, 775

Sodium/liq. ammonia Na/NH_3

Synthesis of acetylene derivatives $CH \rightarrow CR$
s. *9*, 820

Sodium amide $NaNH_2$

Synthesis of dihydrofurans from γ-lactones ←
s. *9*, 822

β-Diketones from carboxylic acid esters $\cdot COCH_2CO \cdot$
s. *4*, 713; silicon compounds s. L. H. Sommer and R. P. Pioch, Am. Soc. *76*, 1606 (1954)

C-Carbalkoxylation $H \rightarrow COOR$
s. *8*, 794

β-Ketocarboxylic acid esters from ketones
s. *3*, 624; s. a. M. Matsui et al., Bull. Chem. Soc. Japan *26*, 194 (1953)

Alkylation of nitriles with p-toluenesulfonic acid esters $CH \rightarrow CR$
s. *9*, 821

Synthesis of amines from aldehydes via α,β-ethylenenitriles ←
s. *8*, 795

Potassium amide KNH_2

Ketones from carboxylic acid esters $COOR \rightarrow COR'$
s. *6*, 748; methoxy compounds s. C. R. Hauser and J. G. Murray, Am. Soc. *77*, 2893 (1955)

Sodium carbonate Na_2CO_3

3,4-Dihydroxy-2-imino-2,5-dihydrofurans from aldehydes ○
s. *9*, 823

Potassium carbonate K_2CO_3

Methylene bridge and hydroxymethylation ←
s. *6*, 749

3-Cyano-2-pyridone ring ○

3-Cyano-2-pyridones s. *6*, 750; 4-cyano-bz-tetrahydro-3-isoquinolones s. H. Henecka, A. *583*, 110 (1953)

Reactions under physiological conditions
s. *8*, 815

Potassium hydrogen carbonate *$KHCO_3$*

Oxazolones – Improved synthesis of azlactones
s. *7*, 776

Sodium acetate and potassium acetate *CH_3COONa and CH_3COOK*

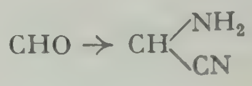
α,β-Ethylenecarboxylic acid amides and unsym. 1,1-di(acylamino) compounds from aldehydes and diacylamines ←
Cation specificity s. *6*, 751

Potassium acetate *CH_3COOK*

Quaternary cyclic enammonium salts ←
s. *8*, 796

Sodium cyanide *NaCN*

α-prim-Aminonitriles from aldehydes
Synthesis with addition of 1 C-atom
s. *9*, 824



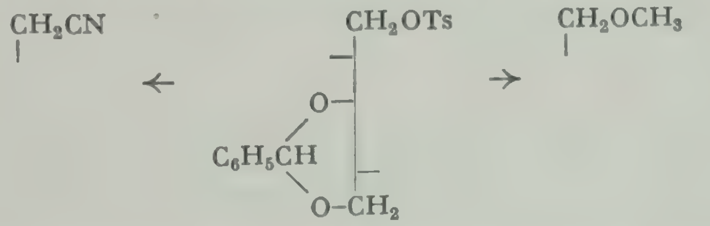
$CHO \rightarrow CH\begin{smallmatrix}NH_2\\CN\end{smallmatrix}$

Sym. hydrazodinitriles from ketones ←
s. *6*, 869; via cyanohydrazones s. *8*, 797

Potassium cyanide *KCN*

Nitriles and ethers from p-toluenesulfonic acid esters ←

3.



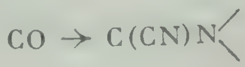
5-Tosyl-1,3-benzylidene-L-arabitol allowed to stand at room temp. for 2 days with 2 moles KCN in methanol → 4,6-benzylidene-2-desoxy-L-galactononitrile (startg. m. f. 181, 224). Y: 93%.

3 days in a soln. of 3 moles Na in methanol → 5-methyl-1,3-benzylidene-L-arabitol. Y: 98%.—With less than 1 mole Na, the 4,5-anhydro derivative is formed.

R. Grewe and H. Pachaly, B. *87*, 46 (1954).

Nitriles only s. *9*, 825

α-Aminonitriles from oxo compounds
s. *6*, 752; *7*, 777



$CO \rightarrow C(CN)N\langle$

Potassium cyanide/hydrochloric acid KCN/HCl

Carboxylactones from ketocarboxylic acids via cyanolactones ○

s. *9*, 826

Sodium hydrogen sulfite $NaHSO_3$

α-Aminonitriles from aldehydes $\mathrm{CHO} \rightarrow \mathrm{CH(CN)NHR}$

s. *6*, 753

Potassium sulfite K_2SO_3

Nitrosulfonic acids from aldehydes and nitroparaffins ←

s. *8*, 798

Sodium salt Na^+

Kostanecki-Robinson reaction ○

Coumarin ring from o-hydroxyketones

s. *9*, 827

Ammonia NH_3

α,β-Ethylene-β-dicarboxylic acids from aldehydes $\mathrm{CHO} \rightarrow \mathrm{C{:}C(COOH)_2}$

s. *7*, 778

Triton B ←

Cinnamylidenemalonic acids from aldehydes $\mathrm{CHO} \rightarrow \mathrm{CH{:}CHCH{:}C(COOH)_2}$

s. *9*, 828

Methylamine CH_3NH_2

1,1-Nitroethylene derivatives from aldehydes $\mathrm{CHO} \rightarrow \mathrm{CH{:}C{\cdot}NO_2}$

s. *6*, 754

1,2-Nitroethylene derivatives from ketones ←

s. *9*, 829

n-Butylamine $n\text{-}C_4H_9NH_2$

1,1-Nitroethylene derivatives from aldehydes $\mathrm{CHO} \rightarrow \mathrm{CH{:}C{\cdot}NO_2}$

s. *6*, 755; s. a. R. V. Heinzelman, Org. Synth. *35*, 74 (1955)

Aniline $C_6H_5NH_2$

α,β-Nitroethylene derivatives from aldehydes $\mathrm{CHO} \rightarrow \mathrm{CH{:}C{\cdot}NO_2}$

s. *9*, 830

Aniline, pyridine $C_6H_5NH_2, C_5H_5N$

α,β-Ethylenecarboxylic acids from aldehydes $\mathrm{CHO} \rightarrow \mathrm{CH{:}CHCOOH}$

Synthesis with addition of 2 C-atoms

s. *9*, 831

tert-Amines ←

α-Acylaminoketones from α-aminocarboxylic acids ←

Dakin-West reaction

s. *6*, 756

Triethylamine *$(C_2H_5)_3N$*

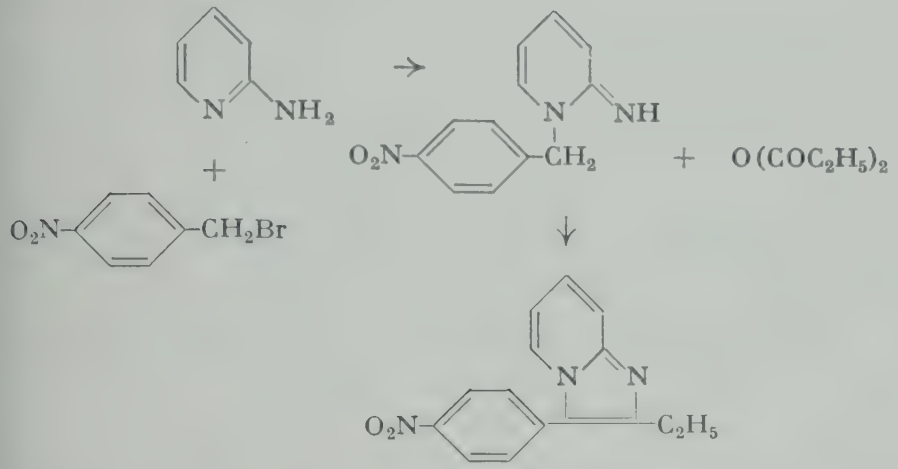
Methine condensation – Oxazolone ring opening ←
s. *6*, 757

Thiomethylation H → CH_2SR
s. *9*, 844

α-Aminocarboxylic acids from oxo compounds via hydantoins ←
s. *9*, 832

Imidazo[1,2-a]pyridines ○

4.



2-Aminopyridine heated with p-nitrobenzyl bromide in dry acetone for 3 hrs. at 65° in a pressure flask → 1-p-nitrobenzyl-2-iminopyridone hydrobromide (Y: 72%) added to a mixture of triethylamine and excess propionic anhydride, and heated 2 hrs. at 130° with occasional shaking → 2-ethyl-3-p-nitrophenylimidazopyridine hydrobromide (Y: 79%). F. e. s. F. Kröhnke and B. Kickhöfen, B. *88*, 1103 (1955).

Triethylamine/acetic anhydride *$(C_2H_5)_3N/(CH_3CO)_2O$*

α,β-Ethylenecarboxylic acids from aldehydes CHO → CH:CHCOOH
s. *4*, 717; s. a. H. Rapoport, R. H. Allen, and M. E. Cisney, Am. Soc. *77*, 670 (1955); DeLos F. DeTar, Org. Synth. *35*, 89 (1955)

Piperidine *$C_5H_{11}N$*

Active methyl and methylene groups ←
s. *7*, 782

10-Arylideneanthrones CHO+H_2C → CH:C
s. *9*, 833

α-Ethylene-β-diketones from β-diketones $C:C(COR)_2$
s. *7*, 339

α,β-Ethylenecarboxylic acids from aldehydes CHO → CH:CHCOOH
Döbner synthesis at low temp. according to Vorsatz
s. *7*, 779

α,β-Ethylenecarboxylic acid esters from aldehydes $CHO \rightarrow CH{:}CHCOOR$
s. *7*, 780; cf. L. Canonica and T. Bacchetti, G. *83*, 1043 (1953)

α,β-Ethylenecarboxylic acid amides from aldehydes $CHO \rightarrow CH{:}CHCONHR$
s. *8*, 799

α,β-Ethylene-α-cyanocarboxylic acid esters from aldehydes $CHO \rightarrow CH{:}C(CN)COOR$
s. *7*, 781

β-Subst. glutaric acids from aldehydes via arylmethylene-bis-acetoacetates ←
s. *6*, 759

Stilbene derivatives – Active methyl groups $CHO + H_3C \rightarrow CH{:}CH$
s. *7*, 782

α-Sulfonyl-α,β-ethyleneketones from β-ketosulfones ←
s. *8*, 800

β-Nitrothioethers from oxo compounds $CHO \rightarrow CH(SR)CH_2NO_2$
s. *7*, 783

Eneheterocyclics ←
s. *8*, 801; *9*, 336

Cyclohexanones ○
s. *7*, 784

Indeno[2,1-b]fluorenes – Cyclohexenones from chalcones
s. *7*, 785

Coumarin ring
s. *6*, 760

Tetrahydrothio-4-pyrones
s. *9*, 834

Morpholine ←
α-Aminocarboxylic acids from aldehydes via hydantoins ←
Synthesis with addition of 2 C-atoms – Eneheterocyclics
s. *6*, 761

Morpholine/pyridine
s. *6*, 762

Pyridine C_5H_5N
Chloral condensation $H \rightarrow CH(OH)CCl_3$
s. *7*, 786

Ketones from carboxylic acids $COOH \rightarrow COR$
s. *9*, 835

Pyridine/aniline s. Aniline/pyridine $C_5H_5N/C_6H_5NH_2$
Pyridine/acetic anhydride $C_5H_5N/(CH_3CO)_2O$
Trimethinecyanines ←
s. *8*, 812

Cuprous cyanide *CuCN*

Nitriles from alcohols OH → CN

s. *7*, 787

Cuprous chloride *CuCl*

s. *7*, 788

Magnesium *Mg*

Synthesis of α,β-ethylenealcohols and dienes from α,β-ethylenealdehydes ←

s. *6*, 764

Ethylmagnesium bromide *C_2H_5MgBr*

Synthesis of hydrocarbons from p-toluenesulfonic acid esters RH+TsOR′ → R·R′

s. *9*, 836

Acetals from orthoformic acid esters C⋮C·CH(OR)$_2$

Synthesis with addition of 1 C-atom

Acetyleneacetals s. *7*, 789; *9*, 837; s. a. N. A. Dobson and R. A. Raphael, Soc. *1955*, 3558

Ketones from carboxylic acid anhydrides C⋮C·COR

Acetyleneketones s. *6*, 765

Zinc chloride *$ZnCl_2$*

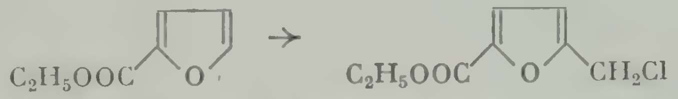
Halogenomethylation H → CH$_2$Hal

s. *7*, 790

Chloromethylation H → CH$_2$Cl

s. *6*, 766

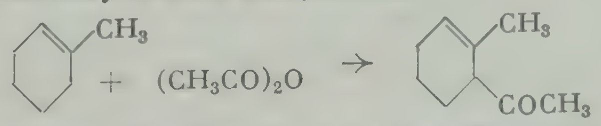
5.



of furans. HCl-gas passed into a mixture of ethyl furan-2-carboxylate, chloroform, paraformaldehyde, and ZnCl$_2$ for 4 hrs. whereby the temp. reaches 30° → ethyl 5-chloromethylfuran-2-carboxylate. Y: 83.1%. F. e. s. O. Moldenhauer et al., A. *580*, 176 (1953).

Ketones from carboxylic acid anhydrides H → COR

6.



Powdered anhydrous ZnCl$_2$ added during 20 min. to a soln. of 1-methylcyclohexene in acetic anhydride whereby the temp. rises to 43°, and stirred for 20 hrs. → 1-methyl-6-acetylcyclohexene. Y: 70%. N. C. Deno and H. Chafetz, Am. Soc. *74*, 3940 (1952); furan derivatives s. H. Williams, P. Kaufmann, and H. S. Mosher, J. Org. Chem. *20*, 1139 (1955).

Ketocarboxylic acids from dicarboxylic acids COOH → COR

s. *7*, 791

α,α-Dialkoxynitriles $C(OR)_3 \rightarrow C(OR)_2CN$
from orthocarboxylic acid esters
s. *7*, 792

Acridine ring – Modified Bernthsen reaction ○
s. *6*, 767

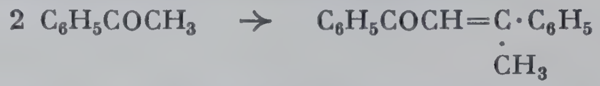
Boric acid/acetic anhydride $HBO_2/(CH_3CO)_2O$

Chalcones via boron complex salts ←
s. *8*, 802

Aluminum alkoxide $Al(OR)_3$

α,β-Ethyleneketones from aldehydes $CHO \rightarrow CH{:}CHCOR$
s. *8*, 803

Dimerization of ketones to α,β-ethyleneketones ←

587. 

$$2\ C_6H_5COCH_3 \rightarrow C_6H_5COCH{=}\underset{\displaystyle CH_3}{C}\cdot C_6H_5$$

Acetophenone and Al-*tert*-butoxide in xylene heated 2 hrs. at 133-137° with stirring under a Vigreux column with distillation of the *tert*-butanol formed → dypnone. Y: 82%. F. e. s. W. Wayne and H. Adkins, Am. Soc. *62*, 3401 (1940).

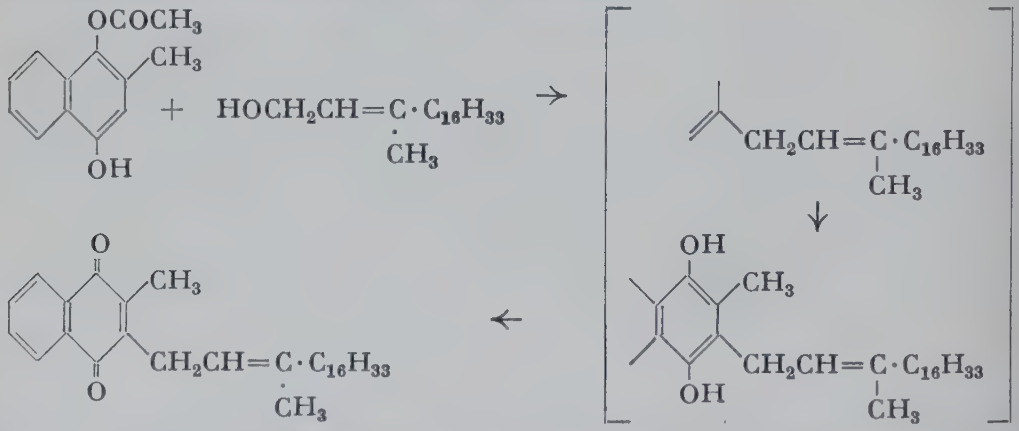
Superfiltrol ←

C-Alkylation of phenols $ArH \rightarrow ArR$
s. *7*, 793

Ketones from carboxylic acid anhydrides $CO{\cdot}O{\cdot}OC \rightarrow COR$
s. *7*, 794

Boron fluoride BF_3

Unidirectional C-alkylation with alcohols $CH \rightarrow CR$

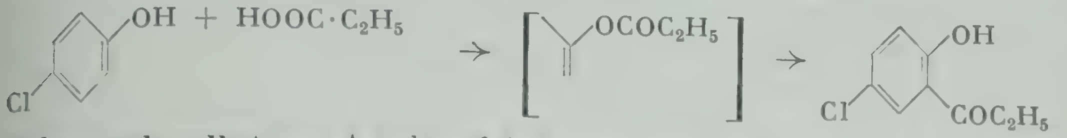
588. 

A soln. of phytol in dioxane added dropwise during 30 min. at 50° to a stirred mixture of excess 2-methyl-1,4-naphthohydroquinone 1 monoacetate, 47%-BF_3-etherate, and dioxane, stirring continued 25 min. at 50°, then worked up whereby the product is treated with aq., then alc.-aq. KOH containing a little Na-hydrosulfite, and finally oxidized to the quinone by shaking 40 min. with Mg-sulfate and Ag-oxide → vitamin K_1. Y: 66.5%. R. Hirschmann, R. Miller, and N. L. Wendler, Am. Soc. *76*, 4592 (1954).

Ketones from carboxylic acids $COOH \rightarrow COR$
s. *6*, 768; s. a. Ng. Ph. Buu-Hoï and J. Séailles, Jr., J. Org. Chem. *20*, 606 (1955)

Phenolketones from phenols via Fries rearrangement

9.



Halogenophenolketones. A soln. of 4-chlorophenol in propionic acid satd. with BF_3, then heated 5 hrs. at 150° in a sealed tube → 4-chloro-2-propionylphenol. Y: 81.5%. F. e. s. K. Kindler and H. Oelschläger, B. *87*, 194 (1954).

Acetoacetylation $H \rightarrow COCH_2COCH_3$
s. *9*, 838

Aluminum chloride *$AlCl_3$*

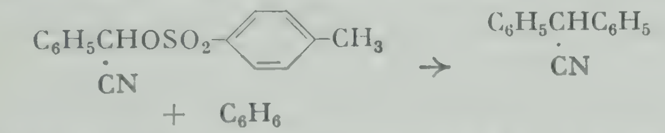
Synthesis of hydrocarbons from p-toluenesulfonic acid esters $ArH + TsOR \rightarrow ArR$
s. *9*, 839

Ketones from carboxylic acid anhydrides $CO{\cdot}O{\cdot}OC \rightarrow COR$
Ketothioethers s. *8*, 804

Synthesis of carboxylic acids from cyanohydrins $C(OH)CN \rightarrow CRCOOH$
s. *7*, 795

Synthesis of nitriles from α-cyanosulfonates $C{\cdot}OSO_2R \rightarrow C{\cdot}R$

1.



A soln. of α-cyanobenzyl p-toluenesulfonate added portionwise during 2 hrs. with stirring to a refluxing mixture of benzene and $AlCl_3$, refluxing continued for 2 hrs. → diphenylacetonitrile. Y: 82.4%. F. e. s. K. Sisido et al., J. Org. Chem. *19*, 1699 (1954).

Synthesis of cyclic ketones from lactones ←
s. *10*, 525

Aluminum chloride/sodium chloride *$AlCl_3/NaCl$*

Annulization – Hydroquinones ○
s. *6*, 769

Aluminum chloride/phosphorus pentachloride *$AlCl_3/PCl_5$*

Aminoketones by Friedel-Crafts synthesis $COOH \rightarrow COR$
Ketones from carboxylic acids
Amines from sulfonic acid amides
s. *8*, 805

Ammonium acetate CH_3COONH_4

β,γ-Ethylenenitriles from ketones ←
via α,β-ethylene-α-cyanocarboxylic acids
s. *7*, 796

Alkylidenecyanoacetic acid esters $C{:}C(CN)COOR$
s. *6*, 770

Pyridine ring synthesis ○
s. *6*, 771; *9*, 840

Acetate ←

Bispidines (3,7-Diazobicyclo[3.3.1]nonanes)
s. *8*, 806

Benzylamine/acetic acid $C_6H_5CH_2NH_2/CH_3COOH$

α-Nitroethylene derivatives and α-nitroalcohols ←
from aldehydes
s. *6*, 772

Piperidinium acetate ←

α-Alkyl-β-ketocarboxylic acid esters ←
from β-ketocarboxylic acid esters
via α-alkylidene-β-ketocarboxylic acid esters
s. *7*, 797

α,β-Ethylenesulfones $C{:}C\cdot SO_2R$
s. *6*, 773; also β-aminosulfones cf. M. Balasubramanian and V. Baliah, Soc. *1954*, 1844; *1955*, 3296

3-Cyano-2-pyridones from ○
ketones via α-hydroxymethyleneketones
s. *8*, 807

Acetamide CH_3CONH_2

α,β-Ethylene-α-cyanocarboxylic acid esters $CHO \rightarrow CH{:}C(CN)COOR$
from aldehydes
s. *8*, 808

Acetic anhydride $(CH_3CH)_2O$
s. a. under Potassium hydroxide, Triethylamine, Pyridine, Boric acid

Chloral condensation $H \rightarrow CH(OH)CCl_3$
s. *10*, 604

Synthesis of ethylene derivatives $CHO+H_2C \rightarrow CH{:}C$
from aldehydes
s. *9*, 848; carbonyl reactivity s. A. P. Phillips, Am. Soc. *76*, 3986 (1954)

Alkylidenemalonic acid esters $CH{:}C(COOR)_2$
s. *8*, 809

Enolethers from orthocarboxylic acid esters ←
Alkoxymethylene compounds s. *8*, 810; heterocyclics s. E. B. Knott, Soc. *1954*, 1482

α-Nitro-β-acylaminocarboxylic acid esters from nitroacetic acid esters and aldehydes or 1,1-di(acylamino) compounds ←
s. *9*, 841

Styrylheterocyclics $CHO+H_3C \rightarrow CH{:}CH$
s. *6*, 135

Unsym. fumaric di-γ-enollactones from γ-enollactones and α,γ-diketocarboxylic acids ←
s. *8*, 811

Trifluoroacetic anhydride $(CF_3CO)_2O$

Ketones from carboxylic acids $COOH \rightarrow COR$
Sulfones from sulfonic acids $SO_2OH \rightarrow SO_2R$
s. *7*, 798

Citrate/hydrochloric acid buffer ←

Synthesis of aminoketones via partially reduced lactams ←
s. *9*, 842

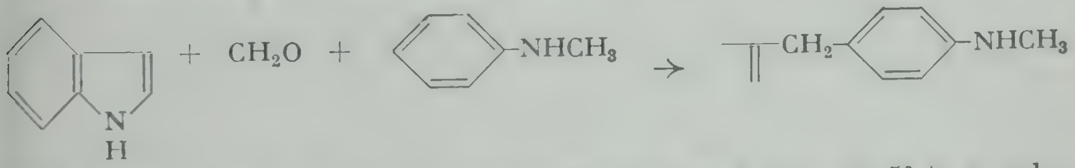
Formic acid *HCOOH*

Cleavage of formaldehyde derivatives with 2,4-dimethylphenol ←
s. *9*, 843

Acetic acid CH_3COOH

α-Methylenecarboxylic acid esters from carboxylic acid esters $CH_2 \rightarrow C{:}CH_2$
s. *8*, 813

Methylene bridge – Anomalous Mannich reaction ←



40%-formalin soln. added dropwise during ca. 5 min. at 5° to a soln. of indole and methylaniline in glacial acetic acid, and allowed to stand 12 hrs. at room temp. in the dark → N-methyl-p-skatylaniline. Y: 24-40%. F. e. s. J. Thesing, H. Mayer, and S. Klüssendorf, B. 87, 901 (1954).

C-Alkylation of ar. amines with carbinols $ArH \rightarrow ArR$
s. *10*, 610

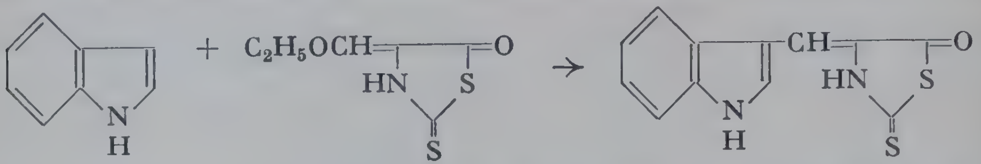
Aminomethylation – Mannich reaction $H \rightarrow CH_2NR_2$
s. *2*, 670; s. a. L. Pichat, M. Audinot, and J. Monnet, Bl. *1954*, 85; E. L. Eliel and M. T. Fisk, Org. Synth. *35*, 78 (1955)

Thiomethylation with formaldehyde and mercaptans or hydroxymethyl thioethers $H \rightarrow CH_2SR$
s. *9*, 844

Iodomethylation H → CH_2I
s. *7*, 799

Synthesis of ethylene derivatives from enolethers C:C(OR) → C:CR′

592.



Indole added to a soln. of 4-ethoxymethylene-2-thio-5-thiazolidone in hot acetic acid, and refluxed 6 hrs. → 4-(3-indolylmethylene)-2-thio-5-thiazolidone. Y: 80%. D. O. Holland and J. H. C. Nayler, Soc. *1953*, 285.

Oxo condensation ←
s. *6*, 774

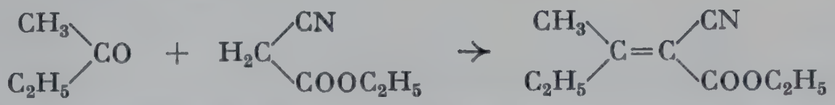
Pyridine ring synthesis via 1,4-dihydropyridines ○
s. *8*, 814

Isatin ring
s. *6*, 775

Aminoacids ←

Aminoacid catalysis of the Knoevenagel condensation $CO+H_2C \rightarrow C:C$
Azeotropic water separation

593.



$$(CH_3)(C_2H_5)CO + H_2C(CN)(COOC_2H_5) \rightarrow (CH_3)(C_2H_5)C{=}C(CN)(COOC_2H_5)$$

A mixture of butanone and ethyl cyanoacetate in benzene containing acetic acid and some ε-aminocaproic acid refluxed 7 hrs. until no more water separates → ethyl s-butylidenecyanoacetate. Y: 79.6%.—Other effective aminoacids are β-alanine, p-aminophenol, and α-aminophenylacetic acid. In addition to efficient condensation, these catalysts allow the elimination of the extraction step usually required in the work-up of the reaction. They are superior to piperidine acetate, and more effective than NH_4-acetate because their loss through amide formation is slower. F. e. and limitations s. F. S. Prout, J. Org. Chem. *18*, 928 (1953); with β-alanine s. Org. Synth. *35*, 6 (1955).

Glycine *H_2NCH_2COOH*

Reactions under physiological conditions
Perkin-Claisen-Knoevenagel condensation
s. *8*, 815

Titanium chloride *$TiCl_4$*

in the Friedel-Crafts reaction

C-Alkylation with alcohols ArH → ArR
s. *10*, 630

Phthalides from o-dicarboxylic acid anhydrides ←
s. *7*, 800

Lead acetate $(CH_3COO)_2Pb$

4-Alkylideneoxazol-5-ones ○
s. *6*, 776

Phosphorus pentoxide P_2O_5

α-Pyrono(5′,6′,3,4)coumarins
s. *6*, 777

Phosphate buffer ←

Endimine ring system
s. *8*, 816

Polyphosphoric acid $H(PO_3H)_xOH$

C-Acylation with carboxylic acids and anhydrides ←
C-Alkylation with alcohols

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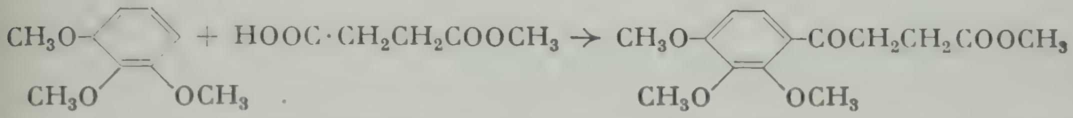
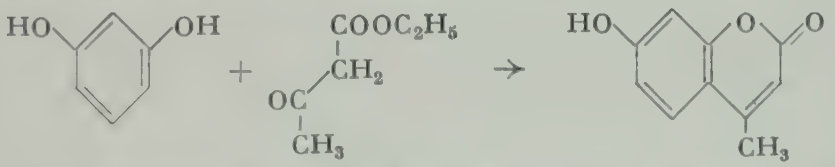


A soln. of trimethylpyrogallol and β-carbomethoxypropionic acid treated with polyphosporic acid at 45° for 2.5 hrs. → methyl β-(2,3,4-trimethoxybenzoyl)propionate. Y: 78.8%.—The product in all cases was the expected Friedel-Crafts adduct; but unlike the $AlCl_3$-catalyzed reaction, no ether cleavage was observed. F. e., also with carboxylic acid anhydrides, C-alkylations with alcohols, and limitations, s. P. D. Gardner, Am. Soc. *76*, 4550 (1954); C-acylation with carboxylic acids s. a. H. R. Snyder and C. T. Elston, Am. Soc. *77*, 364 (1955).

Pechmann-Duisberg coumarin ring synthesis ○



Polyphosphoric acid added at 50° to a soln. of resorcinol in ethyl acetoacetate, and heated 20 min. on a steam bath with stirring → 7-hydroxy-4-methylcoumarin. Y: 98%.—Purer products and better yields are obtained than in the conventional procedure, and the experimental set-up is simple. J. Koo, Chem. & Ind. *1955*, 445.

Phosphoric acid H_3PO_4

Ketones from carboxylic acid anhydrides CO·O·OC → COR
s. *9*, 845

Phosphorus pentachloride/aluminum chloride $PCl_5/AlCl_3$
s. Aluminum chloride/phosphorus pentachloride

Sulfur trioxide SO_3

Nitriles from alcohols OH → CN
Synthesis with addition of 1 C-atom
Labeled compounds s. *8*, 817

Sodium m-nitrobenzenesulfonate ←

Quinolines – Modified Döbner-Miller synthesis ○

s. *6*, 778

Sodium hydroxymethylenesulfonate ←

N-Cyanomethylation NH → NCH_2CN

s. *7*, 801

p-Toluensulfonic acid *TsOH*

Baeyer condensation – Triarylmethanes ←

Reactions with azeotropic water separation s. *9*, 846; also sym. ethers s. *7*, 802

Dihydropyrans from oxo compounds ○

s. *7*, 803

Sulfuric acid H_2SO_4

Synthesis of nitriles from cyanohydrins C·OH → C·R

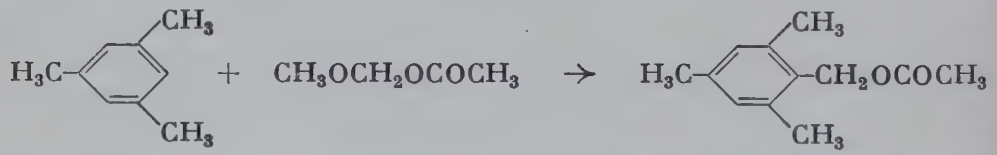
s. *9*, 847

1,1-Diaryl-2-nitroalkanes by condensation

s. *8*, 818

Acoxymethylation H → CH_2OAc

596.



Methoxymethyl acetate and mesitylene dissolved in glacial acetic acid containing concd. H_2SO_4, and stirred 24 hrs. at 27° → 2,4,6-trimethylbenzyl acetate (Y: 23%) and 53% recovered mesitylene.—Polymer formation limits the procedure as a preparative method for the monomeric esters. F. e. s. L. Summers, Am. Soc. *76*, 3481 (1954).

Chloromethylation with di(chloromethyl) ether H → CH_2Cl

s. *8*, 819

Bromomethylation H → CH_2Br

s. *7*, 804; s. a. F. Krausz, Bl. *1953*, C. 51.

Synthesis of hydrocarbons, ethylene derivatives, and sec. alcohols from aldehydes ←

s. *9*, 848

1,1-Disubst. alkanes from ketones CO → $C(Ar)_2$

s. *7*, 805

Arylmethane derivatives ←

s. *7*, 810

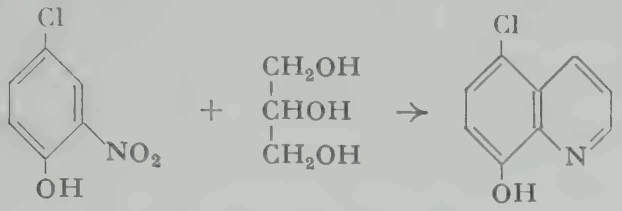
Triarylmethanes from arylaldehydes CHO → $CHAr_2$

s. *6*, 779

2-Pyrones s. *7*, 861 **2,3-Benzopyrones** s. *8*, 820 ○

Quinoline ring from nitro compounds

7.



3 parts concd. H_2SO_4 added slowly with thorough mixing to 1 part p-chloro-o-nitrophenol, 2.5 parts glycerol, and 1.5 parts formic acid, glacial acetic acid, or concd. phosphoric acid, and slowly refluxed with stirring at ca. 140-150° for several hrs. → 5-chloro-8-hydroxyquinoline. Y: 60%. F. e., with lower yields, s. S. J. Das Gupta, J. Indian Chem. Soc. *29*, 711 (1952).

9(H)-Pyrid[3,4-b]indoles – Aromatization
s. *6*, 780

Perchloric acid *$HClO_4$*

Synthesis of ketones from carboxylic acids – anhydrides COR
s. *9*, 849

Ammonium chloride *NH_4Cl*

Aminomethylation – Mannich reaction H → CH_2NR_2
s. *6*, 781

Methylaminomethylsulfonic acids H → $CH_2\overset{+}{N}CH_2SO_3^-$
Inhibition of the aminomethylation
s. *7*, 806

Eneheterocyclics – Rhodanine derivatives ←
s. *8*, 821

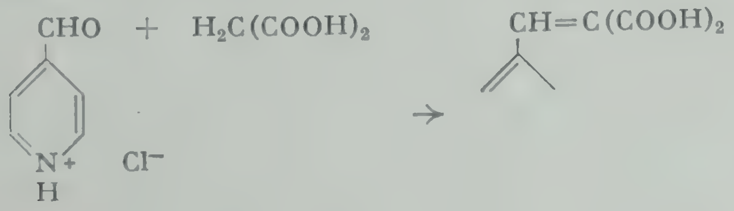
Hydrochlorides ←

Tetraarylmethanes from triarylcarbinols C·OH → C·R
s. *6*, 782

Aminomethylation H → CH_2NR_2
β-Aminoethyl-N-heterocyclics s. *8*, 822; β-aminomethyl-N-heterocyclics s. M. M. and B. L. Robison, Am. Soc. *77*, 457 (1955)

Synthesis of aminoalcohols from amines ←
by combined Mannich-Cannizzaro reaction
s. *7*, 807

1,2-Ethylene-1,1-dicarboxylic acids CHO → CH:C$(COOH)_2$
from aldehydes



4-Formylpyridine hydrochloride, malonic acid, and glacial acetic acid heated 45 min. at 85-90° with stirring → 4-(2,2-dicarboxyvinyl)pyridine hydrochloride. Y: 81%. M. V. Rubtsov, E. S. Nikitskaya, and A. D. Yanina, ЖК. *23*, 963 (1953); C. A. *48*, 8781e.

1,2,3,4-Tetrahydroisoquinolines from amines ○
Pictet-Spengler ring closure
Reactions under physiological conditions
s. *8*, 823

Quinolizine ring
s. *4*, 740; s. a. K. T. Potts and R. Robinson, Soc. *1955*, 2675

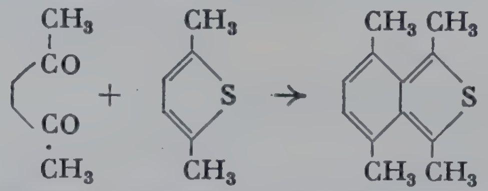
Hydrofluoric acid *HF*

Methylene bridge $2\,RH \rightarrow R\cdot CH_2\cdot R$
s. *7*, 808

C-Alkylation of phenols $ArH \rightarrow ArR$
s. *7*, 809

Benzene ring from γ-diketones ○

599.



Commercial 96-100%-HF added with cooling to a mixture of 2,5-dimethylthiophene and acetonylacetone in an autoclave, and heated 3 hrs. in a boiling water bath with occasional shaking → 1,3,4,7-tetramethylisothianaphthene. Y: 42%. O. Dann, M. Kokorudz, and R. Gropper, B. *87*, 140 (1954).

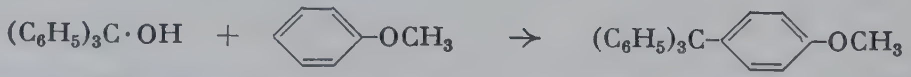
One-step indanone ring synthesis
s. *6*, 819

Hydrochloric acid *HCl*

Arylmethane derivatives $C\cdot OH \rightarrow C\cdot Ar$
s. *7*, 810

Tritylation of ar. compounds

600.



A mixture of triphenylcarbinol, a slight excess of anisole, and HCl refluxed 16 hrs. → p-methoxytetraphenylmethane. Y: 89%. F. e., also with triphenylchloromethane, and limitations, s. C. A. MacKenzie and G. Chuchani, J. Org. Chem. *20*, 336 (1955).

1,1-Disubst. alkanes from ketones $CO \rightarrow CR_2$
s. *6*, 783; furan derivatives s. R. G. Ackman, W. H. Brown, and G. F. Wright, J. Org. Chem. *20*, 1147 (1955)

Introduction of methyl groups into ar. rings via chloromethylation $H \rightarrow CH_3$
s. *8*, 824

Aminomethylation – Mannich bases ←
β-Alkoxyketones from ketones via β-aminoketones
Hofmann degradation of quaternary ammonium salts
s. *7*, 811

Aminomethylation – Sulfonic acid amides $H \rightarrow CH_2NHSO_2\cdot$
s. *8*, 825

Benzene ring by trimerization ○
s. *9*, 850

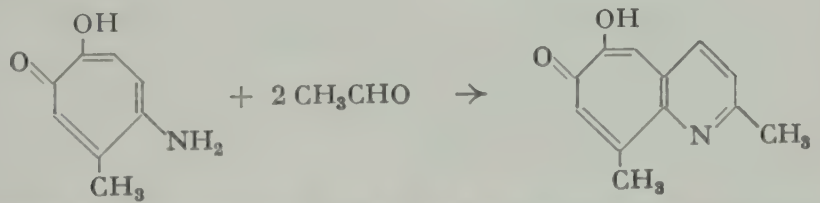
Furan ring synthesis
s. *7*, 814

Benzofurans via 3-halogenocoumarins
Perkin transformation
s. *6*, 784

Xanthenes
s. *8*, 826

Döbner-Miller synthesis
Quinaldines
s. *9*, 851

1.



Pyridino[2,3-d]tropolones. 0.3 g. γ-Amino-β-methyltropolone, 0.4 g. paraldehyde, and concd. HCl refluxed 0.5 hr. → 0.5 g. 2,9-dimethylpyridino[2,3-d]tropolone. P. Akroyd, R. D. Haworth, and P. R. Jefferies, Soc. *1954*, 286.

Dihydropyrimidines
s. *9*, 852

Iron/cupric sulfate/sulfuric acid $Fe/CuSO_4/H_2SO_4$
Isocyclics from quinones
s. *9*, 853

$FeSO_4/HBO_2$
Ferrous sulfate/boric acid
Skraup-Cohn quinoline synthesis
s. *7*, 812

$FeSO_4/C_6H_5NO_2$
Ferrous sulfate/nitrobenzene
Skraup quinoline synthesis
s. *6*, 785

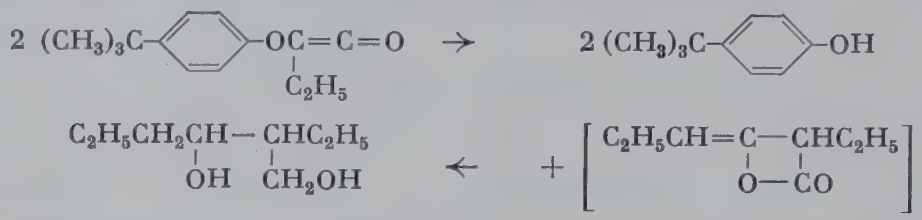
Ferric chloride *$FeCl_3$*

Ketones from carboxylic acid anhydrides CO·O·OC → COR
s. *7*, 813

Nickel *Ni*

Glycols from aryloxyketenes by reductive dimerization ←

602.

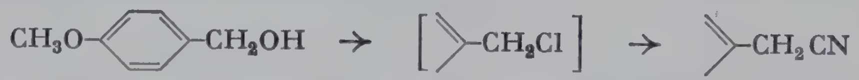


p-*tert*-Butylphenoxyethylketene hydrogenated 4-6 hrs. with Raney-Ni in petroleum ether at 200-350° and 1500-3500 p. s. i. → 3-hydroxymethyl-4-heptanol (Y: 65%) and p-*tert*-butylphenol (Y: 37%). F. e. s. C. M. Hill et al., Am. Soc. *75*, 1084 (1953).

Via intermediates *v.i.*

Nitriles from alcohols via chlorides $CH_2OH \rightarrow CH_2CN$

603.



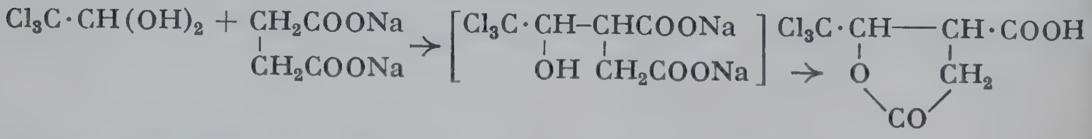
Anhydrous HCl bubbled rapidly for 1 hr. into a soln. of p-methoxybenzyl alcohol in benzene contained in a separatory funnel, the concd. hydrochloric acid which separates drawn off, the benzene soln. washed with water and $NaHCO_3$ until no longer acidic, then added during 40 min. to a boiling stirred aq. soln. of NaCN, stirring and refluxing continued 5 hrs. → p-methoxyphenylacetonitrile. Y: 80-83%. J. H. Burckhalter et al., Am. Soc. *76*, 4112 (1954).

Diene synthesis
s. *6*, 786

Furan ring synthesis ○
s. *7*, 814

Synthesis of lactones from aldehydes ←

604.



Chloral condensation. Acetic anhydride added slowly with stirring to a mixture of powdered anhydrous chloral, the flask placed in an oil bath preheated to 130°, the temp. increased to 140° over a 25 min. period, kept 65 min. at ca. 140° whereby vigorous stirring is maintained throughout, and the crude product treated with concd. HCl → trichloromethylparaconic acid. Y: 72%. H. P. Kato and S. R. Dickman, Biochem. Prep. *3*, 52 (1953).

Benzopyrans from coumarins ←
s. *7*, 815

Nitrogen ↑ CC⇅N

Without additional reagents *w.a.r.*

Arylation with N-nitrosoacylamines H → Ar
s. *1*, 604; s. a. Y. Ahmad and D. H. Hey, Soc. *1954*, 4516; C. S. Rondestvedt, Jr., and H. S. Blanchard, Am. Soc. *77*, 1769 (1955)

Replacement of hydrogen by methyl via aminomethyl compounds H → CH_3
s. *8*, 827

Tert. amines from diazo compounds ←
s. *9*, 854

C-β-Acylethylation – 1,5-Diketones H → CH_2CH_2COR
s. *8*, 828

C-Cyanomethylation H → CH_2CN
s. *9*, 855

Ketones from aldehydes ←
s. *7*, 816

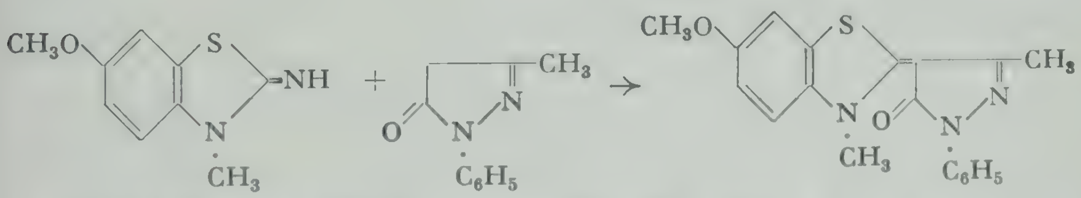
Synthesis of oxo compounds from hydrocarbons and amidines via azomethines CH → C·COR
s. *9*, 857

α,β-Ethylene-α-cyanocarboxylic acid esters from 1,1-di(acylamino) compounds $C(NHAc)_2 \rightarrow C{:}C(CN)COOR$
s. *9*, 858

Enamines from formamidines ←
s. *7*, 817

Cyanines $C{:}NH + H_2C \rightarrow C{:}C$

5.



2-Imino-6-methoxy-3-methylbenzothiazoline (prepn. s. 293) fused with 1-phenyl-3-methyl-5-pyrazolone at 150-155°/10-15 mm. for 2 hrs. → 4-(3′-methyl-6′-methoxybenzothiazolin-2′-ylidene)-1-phenyl-3-methyl-5-pyrazolone. Y: 90%. F. e., also monomethinecyanines, s. G. M. Oksengendler, Ж. *23*, 135 (1953); C. A. *48*, 672e.

Synthesis of cyclobutanones and α,β-ethyleneketones from azibenzils ←
s. *8*, 829

Pyrrole synthesis ○
s. *8*, 830

Oxazolones from acylisocyanates and diazomethane
s. *6*, 787

Irradiation ←

Two-step azulene synthesis ←
Ring expansion of isocyclics – Dehydrogenation
s. *9*, 859

Sodium *Na*

1-Subst. isoquinolines ←
via 2-acyl-1,2-dihydroisoquinaldonitriles (Reissert compounds)
Syntheses with tert. amines
s. *7*, 818

Sodium hydride *NaH*

Synthesis of α-aminocarboxylic acids with tert. amines $CH_2NR_2 \rightarrow CH_2CH(NH_2)COOH$
s. *9*, 860

Sodium hydroxide *NaOH*

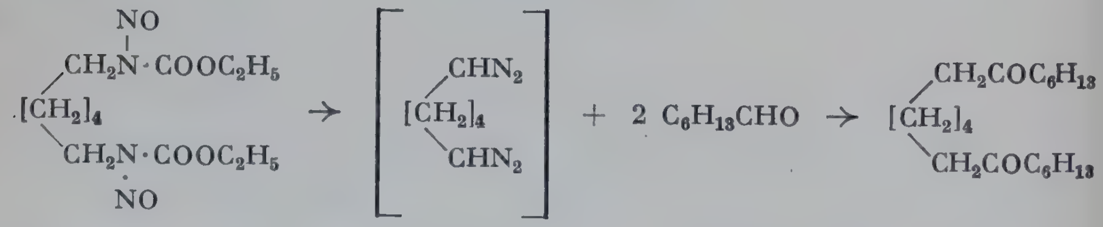
N-Carboxymethylation ←
s. *6*, 788

Syntheses with tert. amines ←
s. *6*, 789; with methyl instead of ethyl ester s. H. *292*, 283 (1954); s. a. H. N. Rydon and J. C. Tweddle, Soc. *1955*, 3499

C-β-Acylethylation $H \rightarrow CH_2CH_2COR$
γ-Nitroketones from tert. amines
s. *9*, 861

Reactions with diazo compounds ←
Synthesis of ketones from aldehydes

606.



A pellet of NaOH added at 2° to a soln. of N,N′-dinitroso-N,N′-dicarbethoxy-1,6-diaminohexane and n-heptaldehyde in abs. ethanol, whereupon the temp. rises slowly to 40° and then drops, the NaOH-pellet removed when the soln. has reached room temp., and the product isolated → 7,14-eicosanedione. Y: 72%. F. e. and reactions s. C. M. Samour and J. P. Mason, Am. Soc. *76*, 441 (1954).

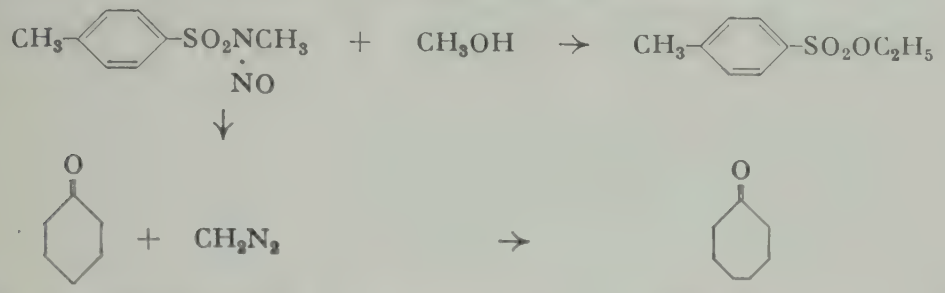
Borsche synthesis of N-heterocyclics ○
s. *1*, 610; s. a. H. E. Baumgarten and A. L. Krieger, Am. Soc. *77*, 2438 (1955)

Potassium hydroxide *KOH*

Ring expansion of isocyclics with diazo compounds ←

Diazo compounds from N-nitrososulfonic acid amides

07.



Prepn. of diazomethane. A soln. of KOH in water-alcohol (1:1) added dropwise at 10-20° with gentle stirring during 2 hrs. to a mixture of cyclohexanone, p-tolylsulfonylmethylnitrosamide (prepn. s. 250), ethanol, and water, stirring continued for 30 min., acidified with HCl to litmus, and the product isolated via the bisulfite adduct → cycloheptanone. Y: 33-36%.—p-Tolylsulfonylmethylnitrosamide is a useful substance for the prepn. of diazomethane (Org. Synth. *34*, 96; R. *73*, 229). T. J. de Boer and H. J. Backer, Org. Synth. *34*, 24 (1954); R. *73*, 589 (1954).

Sodium/alcohol *NaOR*

Syntheses with tert. amines – α-Aminocarboxylic acids
s. *3*, 665; s. a. F. C. Uhle and S. H. Robinson, Am. Soc. *77*, 3544 (1955)

Isatylidene compounds ←
s. *9*, 862

Synthesis of aliphatic nitro compounds from quaternary ammonium salts ←
s. *8*, 831

Isocyclics from quaternary ammonium salts ○
s. *7*, 819/20

Modified Robinson-Mannich base procedure
Tert. amines as intermediates
s. *7*, 869

Potassium/alcohol *KOR*

Cyclohexenones from β-aminoketones
s. *6*, 790; *9*, 863; to *6*, 790 s. a. Soc. *1955*, 3348; in aq. alc. KOH cf. W. F. Newhall et al., Am. Soc. *77*, 5646 (1955)

Phenyllithium *C_6H_5Li*

Introduction of aldehyde groups into ar. rings H → CHO
s. *9*, 864

Nitriles from organometallic compounds ←
Replacement of hydrogen by cyano groups
s. *9*, 865

Alkali cyanide ←

Carboxylic acids from quaternary ammonium salts via nitriles $\overset{+}{N}R_3 \rightarrow COOH$

Synthesis with addition of 1 C-atom

s. *9*, 866

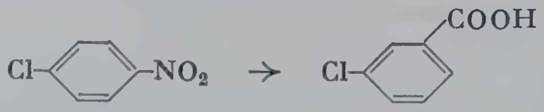
Potassium cyanide *KCN*

von Richter reaction – Improved procedure ←

Position shift of substituents of isocyclics

Carboxylic acids from nitro compounds

608.

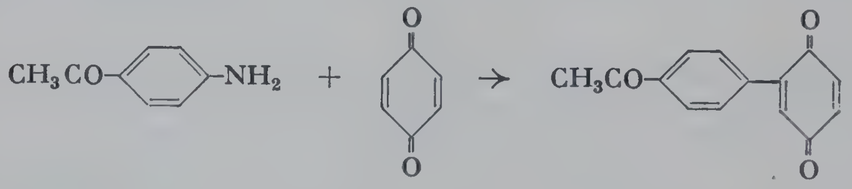


p-Chloronitrobenzene refluxed 48 hrs. with excess KCN in 48%-alcohol → m-chlorobenzoic acid. Y: 40%. F. e. s. J. F. Bunnett et al., Am. Soc. *76*, 5755 (1954).

Sodium nitrite *$NaNO_2$*

Arylation of quinones ←

609.



Aq. $NaNO_2$ added with stirring during 5 min. to p-aminoacetophenone, chopped ice, and HCl, stirring continued for 15 min., the soln. then added slowly during 0.5-1 hr. below 15° to a mixture of quinone, $NaHCO_3$, and ice-water, allowed to warm to room temp. and stirring continued for an additional hr. → crude 2-p-acetylphenylquinone. Y: 96-98%. G. A. Reynolds and J. A. VanAllan, Org. Synth. *34*, 1 (1954).

Diethylamine *$(C_2H_5)_2NH$*

Reactions of nitroacetic acid ester ←

Salts of aci-α,γ-dinitroglutaric acid esters from nitroacetic acid ester and azomethines and aldehydes

s. *9*, 856

Copper *Cu*

α,β-Ethylene-γ-diketones from α-diazoketones – Dimerization $2 \cdot COCHN_2 \rightarrow \cdot COCH{:}CHCO \cdot$

with Cu s. *9*, 867; with CuO cf. I. Ernest, Coll. Czech. Chem. Communs. *19*, 1179 (1954)

α-Halogenocarboxylic acid esters from halides and diazoacetic ester $Hal \rightarrow CHHalCOOR$

s. *7*, 821

Cupric sulfate *$CuSO_4$*

Synthesis of oxo compounds from amines and oximes $NH_2 \rightarrow CO$
s. *9*, 868

Carboxylic acids from amines via nitriles $NH_2 \rightarrow COOH$
Synthesis with addition of 1 C-atom
s. *8*, 832

α-Halogenocarboxylic acid esters $Hal \rightarrow CHHalCOOR$
from halides and diazoacetic ester
s. *7*, 821

Cyclopropane ring from diazo compounds ○
s. *8*, 833

Cupric chloride *$CuCl_2$*

Diazo coupling ←
s. *6*, 792

Zinc chloride *$ZnCl_2$*

Synthesis of α-ketocarboxylic acids ←
and α-keto-γ-lactones from ethyl cyanoformate
s. *8*, 834

Hexamethylenetetramine *$C_6H_{12}N_4$*

Phenolaldehydes from phenols $H \rightarrow CHO$
via sec. amines and azomethines
Duff reaction
s. *8*, 835

Acetic anhydride *$(CH_3CO)_2O$*

Syntheses with 1,1-di(acylamino) compounds ←
s. *9*, 841

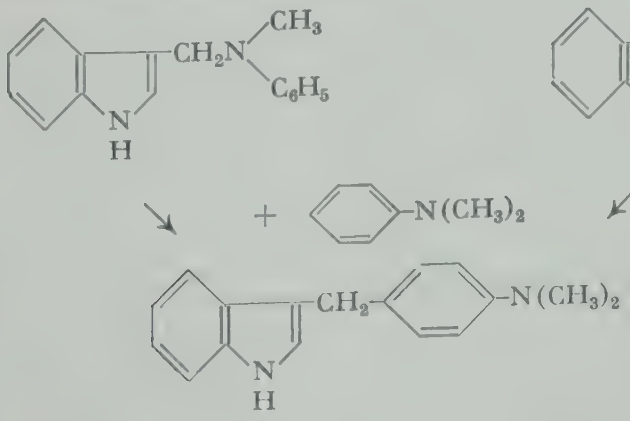
Formic acid *$HCOOH$*

Cleavage of formaldehyde derivatives ←
with 2,4-dimethylphenol
s. *9*, 869

Acetic acid *CH_3COOH*

C-Alkylation of ar. amines $ArH \rightarrow ArR$
with Mannich bases and carbinols

0.



A soln. of 0.01 mole N-methyl-N-phenylskatylamine or 3-hydroxymethylindole in ethanol added dropwise with vigorous stirring at 5° during 40 min. to a mixture of 0.1 mole dimethylaniline and glacial acetic acid, allowed to stand overnight → N,N-dimethyl-p-skatylaniline. Crude Y: ca. 100%. J. Thesing and H. Mayer, B. *87*, 1084 (1954).

Arylation of ferrocenes with diazonium salts

611.
$$C_6H_5\overset{+}{N_2} + C_5H_5{-}Fe{-}C_5H_5 \rightarrow C_6H_5C_5H_4{-}Fe{-}C_5H_5$$

Benzenediazonium sulfate in as small a volume of water as convenient dropped rapidly at room temp. under N_2 into a stirred soln. of ferrocene (biscyclopentadienyliron(II)) in glacial acetic acid, at the end of the reaction (testing a small sample with alkaline β-naphthol) or next morning water added followed by sufficient titanous sulfate soln. to reduce any ferricinium salt present, and extracted with ether → phenylferrocene (Y: 66%), diphenylferrocene (Y: 9%), and 41% recovered startg. m. F. e. s. G. D. Broadhead and P. L. Pauson, Soc. *1955*, 367; cf. V. Weinmayr, Am. Soc. *77*, 3012 (1955).

Fischer indole ring synthesis ○
s. *4*, 761; azabenzazulenes s. C. W. Muth, D. O. Steiniger, and Z. B. Papanastassiou, Am. Soc. *77*, 1006 (1955)

Polyphosphoric acid *$H(PO_3H)_xOH$*
s. *9*, 870; cf. H. N. Rydon and J. C. Tweddle, Soc. *1955*, 3499

Phosphorus oxychloride *$POCl_3$*

Aldehyde synthesis H → CHO

with dimethylformamide
s. *9*, 871; N-heterocyclics s. G. F. Smith, Soc. *1954*, 3842; R. M. Silverstein et al., J. Org. Chem. *20*, 668 (1955)

with N-alkylformanilide

Introduction of methyl groups into ar. rings via aldehydes
s. *8*, 836; introduction of methyl groups s. a. Ng. Ph. Buu-Hoï and D. Lavit, Soc. *1955*, 2776; J. Org. Chem. *20*, 1191 (1955)

Synthesis of ketones from carboxylic acid amides H → COR
s. *9*, 872

Phosphorus oxybromide *$POBr_3$*

Aldehyde synthesis with N-alkylformanilide H → CHO
s. *6*, 793

Sulfuric acid *H_2SO_4*

Fischer indole ring synthesis ○
s. *7*, 452

Hydrochloric acid *HCl*

Fischer-Zerweck aldehyde synthesis H → CHO
s. *9*, 873

Fischer indole ring synthesis ○
s. *6*, 794

Halogen ↑

CC⇅Hal

Without additional reagents

w.a.r.

Condensation with elimination of hydrogen halides RHal+HR′ → R·R′
Dipyrrylmethanes s. *7*, 822

1,1,2,2-Tetraarylethanes $Ar_2CHCHAr_2$
s. *9*, 874

Synthesis of α,β-ethyleneketones from carboxylic acid chlorides COCl → COCH:C
s. *9*, 875

Malonic acid esters from carboxylic acid bromides via diazo compounds COBr → $CH(COOR)_2$
s. *6*, 795

2-Acylamino-1,3-diols from carboxylic acids via α-bromocarboxylic acid bromides, α-diazo-β-keto-γ-bromocarboxylic acid esters, and α-amino-β-ketocarboxylic acid esters ←
s. *9*, 876

α-Diazoketones from carboxylic acids via carboxylic acid chlorides COOH → $COCHN_2$
s. *9*, 877

Coumarandiones
s. *8*, 837

Pyrrolidinetriones
s. *7*, 823

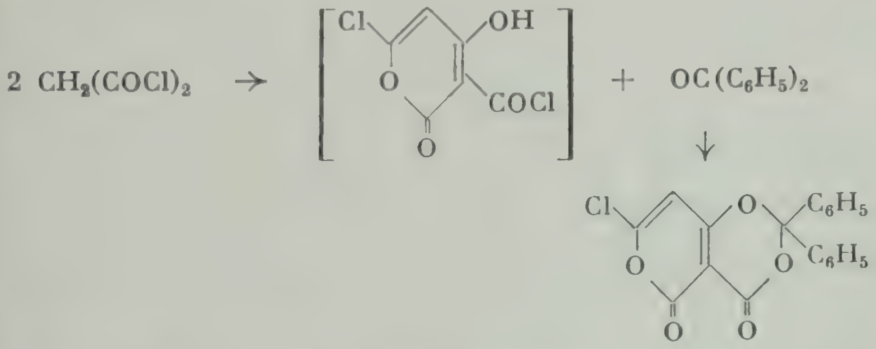
○

Synthesis of quinolinium salts
s. *6*, 797

Thianaphthenes
s. *6*, 796

4,5-Dioxopyrano[4,3-d]-m-dioxins from malonyl chloride and ketones

2.



Malonyl chloride and benzophenone heated at 100° until HCl-evolution ceases → 7-chloro-4,5-dioxo-2,2-diphenylpyrano[4,3-d]-m-dioxin. Y: 82%. F. e. s. S. J. Davis and J. A. Elvidge, Soc. *1952*, 4109.

Lithium

Li

Synthesis of hydrocarbons from halides RHal → R·R′
s. *6*, 798; inverse addition of organometallic reagents s. *9*, 878

Lithium/copper salt ←

Synthesis of tropones from tropolones ←
s. *8*, 838

Lithium/mercuric iodide s. Mercuric iodide/lithium *Li/HgI_2*

Sodium *Na*

Methyl ketones from carboxylic acids via ←
carboxylic acid chlorides and acylmalonic acid esters
s. *7*, 583

Synthesis of ketones and β-ketocarboxylic acid esters ←
from carboxylic acid chlorides
with 2-tetrahydropyranyl malonates
s. *8*, 839

Tetronic acids from α-bromocarboxylic acid bromides ○
s. *8*, 840

Sodium/potassium isopropoxide *Na/KOR*

Synthesis of hydrocarbons $RHal + HR' \rightarrow R\cdot R'$
s. *9*, 879

Potassium *K*

Alkylation of α-phosphonocarboxylic acid esters CH → CR
s. *7*, 824

Sodium hydride *NaH*

Synthesis of hydrocarbons via 1,1-disulfones ←
s. *9*, 880

Dialkylation of ketones $COCH_2 \rightarrow COCR_2$
s. *7*, 825

Alkylation of nitriles CHCN → CRCN
s. *7*, 826

Synthesis of ketones from ←
carboxylic acid chlorides with tert-butyl malonates
Alkylation of malonic acid esters
Blocking of carboxyl groups
s. *9*, 881; alkylation of malonic acid esters s. a. N. L. Drake and W. B. Tuemmler, Am. Soc. *77*, 1204 (1955)

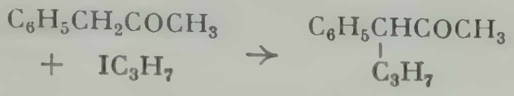
Sodium hydride as condensing agent ←
in the synthesis of α-aminocarboxylic acids
s. *8*, 841

Darzens-Claisen reaction
Aldehydes from ketones via glycidic acid esters CO → CHCHO
Synthesis with addition of 1 C-atom
s. *8*, 842

Sodium hydroxide *NaOH*

Alkylation of ketones

COCH → COCR



$$C_6H_5CH_2COCH_3 + IC_3H_7 \rightarrow C_6H_5\underset{C_3H_7}{\underset{|}{C}}HCOCH_3$$

Phenylacetone added in one portion to powdered NaOH, vigorously stirred without cooling for 15 min., then n-propyl iodide added dropwise at 30-35° during 1 hr., stirred ca. 2 hrs. without cooling, when the evolution of heat diminishes heated, cautiously at first, on a steam bath for 3 hrs. → 1-phenyl-1-n-propylacetone. Y: 71%.—This procedure is simple since a solvent is not required and no special precautions to exclude moisture must be taken. F. e. s. E. M. Schultz et al., Am. Soc. *75*, 1072 (1953).

Anomalous Reimer-Tiemann reaction ←

s. *8*, 843

Potassium hydroxide s. under Potassium iodide and Copper *KOH*

Sodium/alcohol *NaOR*

Simultaneous C- and O-methylation ←

s. *9*, 882

Alkylation

of β-ketocarboxylic acid esters ·HC(COR′)COOR″→·RC(COR′)COOR″

s. *9*, 933

of α-cyanocarboxylic acid esters ·HC(CN)COOR → ·R′C(CN)COOR

s. *6*, 802

of 2-imidazolinyl-2-acetic acid esters

2-Alkyl-2-imidazolines from 2-imidazolinyl-2-acetic acid esters

s. *8*, 844

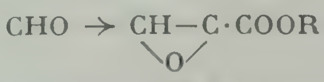
Syntheses with benzyl esters ←

Ketones, ketocarboxylic acid esters, and cyanoketones from carboxylic acid chlorides

s. *7*, 827; γ-ketocarboxylic acids s. J. E. Davies, F. E. King, and J. C. Roberts, Soc. *1955*, 2782

Glycidic acid esters from aldehydes

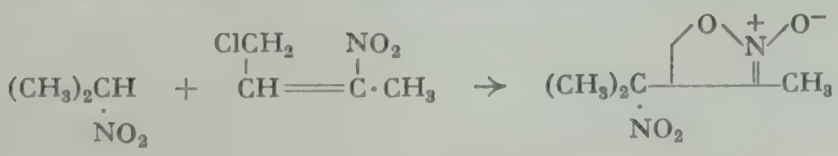
Darzens-Claisen reaction



$$CHO \rightarrow CH\text{—}C\cdot COOR \; (\text{—}O\text{—})$$

s. *1*, 634; s. a. H. Henecka, A. *583*, 110 (1953); synthesis of ketones from aldehydes via glycidic acid esters s. a. T. C. Myers et al., Am. Soc. *77*, 5655 (1955)

Isoxazoline oxides from 3-nitro-2,3-ethylenehalides ○

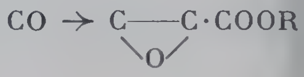


2-Nitropropane converted into the nitronate by slow addition to a cooled soln. of Na in abs. ethanol, cooled to −20°, 1-chloro-3-nitro-2-butene (prepn. s. 649) added rapidly, and stirred 24 hrs. → 3-methyl-4-(2-nitro-2-propyl)isoxazoline oxide. Y: 36%. H. Shechter and F. Conrad, Am. Soc. *76*, 2716 (1954).

Synthesis of dicarboxylic acid esters
from cyclic β-ketocarboxylic acid esters
Hydrolytic ring opening of isocyclics
s. *9*, 883

Sodium ethoxide

Glycidic acid esters from oxo compounds
Darzens-Claisen reaction
s. *8*, 845


$CO \rightarrow C\text{—}C\cdot COOR$ (with O bridging the two C)

Sodium tert-amoxide

Alkylation of ketones COCH → COCR
s. *3*, 671; s. a. Bl. *1954*, 690; A. ch. *8*, 709 (1953)

Sodium compound ←

Synthesis of hydrocarbons via 1,1-disulfones ←
s. *9*, 880

Acylmalonic acid esters $RCOCH(COOR')_2$
s. *8*, 846

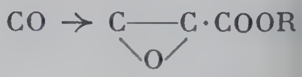
Potassium isobutoxide *KOR*

Cycloalkanecarboxylic acids by malonic acid synthesis ○
s. *9*, 884; with Na/ethanol cf. S. F. Birch et al., J. Org. Chem. *20*, 1178 (1955)

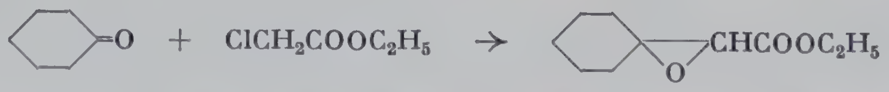
Potassium tert-butoxide

Disubst. from monosubst.
malonic acid esters $HRC(COOR)_2 \rightarrow R'RC(COOR)_2$
s. *7*, 828

Glycidic acid esters from ketones
Darzens-Claisen reaction


$CO \rightarrow C\text{—}C\cdot COOR$ (with O bridging the two C)

615.



A soln. of K in *tert*-butanol added dropwise under N_2 with stirring during ca. 1.5 hrs. at 10-15° to a mixture of cyclohexanone and ethyl chloroacetate, stirring continued 1-1.5 hrs. at ca. 10°, then most of the *tert*-butanol removed by distillation at a bath temp. of 100° and reduced pressure → ethyl β,β-pentamethyleneglycidate. Y: 83-95%. R. H. Hunt, L. J. Chinn, and W. S. Johnson, Org. Synth. *34*, 54 (1954).

Potassium isopropoxide/sodium *KOR/Na*
s. Sodium/potassium isopropoxide

Butyllithium *C_4H_9Li*

Synthesis of hydrocarbons from halides RHal+HR′ → R·R′
Metalation of thiophenes s. *9*, 885

Syntheses with lithium alkenyls
Halogen-metal interconversion method

Carboxylic acids from halides Hal → COOH
Retention of configuration s. *8*, 847

α,β-Acetylenecarboxylic acids from α,β-ethylenehalides ←
s. *9*, 886

Phenyllithium *C_6H_5Li*

Synthesis of hydrocarbons from halides
Metalation RHal+HR′ → R·R′
s. *9*, 887

Selective replacement of halogen by alkyl RHal+HalR′ → R·R′
s. *8*, 848

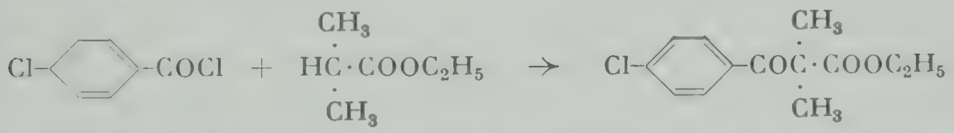
Alkylation of Reissert compounds CH → CR
s. *9*, 581

Synthesis of prim. alcohols from formaldehyde with preceding alkylation ←
s. *8*, 849

Dimerization of halides – Isocyclics from halides ←
s. *9*, 966

Triphenylmethylsodium *$(C_6H_5)_3C\cdot Na$*

β-Ketocarboxylic acid esters from carboxylic acid esters COCl → COC·COOR



Ethyl isobutyrate added to a stirred ethereal soln. of triphenylmethyl-Na, when the red color of the reagent has faded to light orange (usually within 5 min.; within 1 min. in the presence of traces of mercury) p-chlorobenzoyl chloride in dry ether added rapidly, and stirring continued for 2 hrs. → ethyl p-chlorobenzoyldimethylacetate. Y: 79%. F. e. s. D. F. Thompson, P. L. Bayless, and C. R. Hauser, J. Org. Chem. *19*, 1490 (1954).

Lithium diethylamide *$(C_2H_5)_2NLi$*

Alkylation of nitriles CHCN → CRCN
s. *7*, 829

Sodium/liq. ammonia *Na/NH_3*

Acetylene derivatives from halides Hal → C⋮CH
Improved procedure s. *7*, 830

Sodium amide *$NaNH_2$*

Synthesis of acetylene derivatives from halides ←
s. *9*, 888

Alkylation CH → CR

of nitriles with migration of a carbon-carbon bond
s. *7*, 831

***α*-Side chain alkylation of pyridines**
s. *8*, 851

Partial alkylation of diacetylene derivatives Hal → C⋮CR
s. *6*, 799

***α*-Substitution of sulfones** $CHSO_2R \rightarrow CR'SO_2R$
s. *8*, 850

Acetylenecarboxylic acids from 1,2-dihalides ←
s. *7*, 832

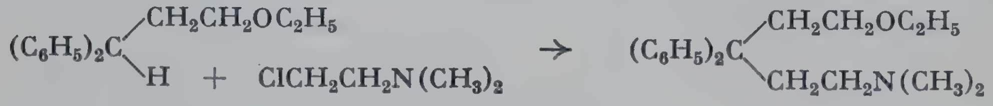
Piperidinium ring synthesis ○
s. *6*, 800

Potassium amide *KNH_2*

Polymethylenebipyridines ←
s. *9*, 889

Alkylation CH → CR

617.



$$(C_6H_5)_2C\begin{matrix}CH_2CH_2OC_2H_5\\ H\end{matrix} + ClCH_2CH_2N(CH_3)_2 \rightarrow (C_6H_5)_2C\begin{matrix}CH_2CH_2OC_2H_5\\ CH_2CH_2N(CH_3)_2\end{matrix}$$

3,3-Diphenyl-1-ethoxypropane added to a stirred soln. of KNH_2 in liq. NH_3, stirring continued for 0.5 hr., then *β*-dimethylaminoethyl chloride slowly added, and the product isolated when all the NH_3 has evaporated → 5-ethoxy-3,3-diphenyl-N,N-dimethylamylamine (startg. m. f. 16). Y: 80%. F. e. s. N. Sperber, M. Sherlock, and D. Papa, Am. Soc. *75*, 1122 (1953); alkylation of tert. amines s. C. R. Hauser et al., J. Org. Chem. *20*, 1119 (1955).

of *α,β*-ethylenecarboxylic acids with migration of carbon-carbon double bonds
s. *7*, 833

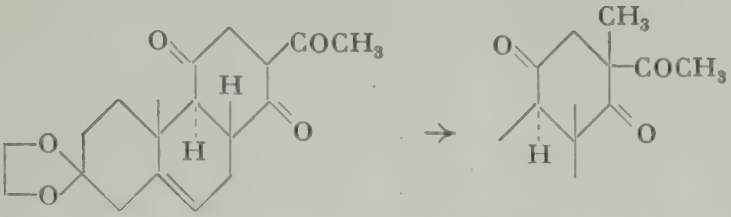
of *β*-di(enolethers)
s. *8*, 852

Ketones from carboxylic acid chlorides COCl → COR
s. *6*, 801

Potassium carbonate *K_2CO_3*

Alkylation CH → CR

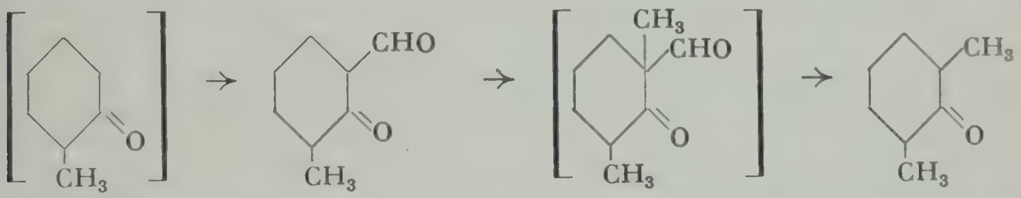
18.



4b-Methyl-2-acetyl-7-ethylenedioxy-1,2,3,4,4aα,4b,5,6,7,8,10,10aβ-dodecahydrophenanthrene-1,4-dione and methyl iodide added to a suspension of anhydrous K-carbonate in acetone, and stirred at room temp. overnight → 2,4b-dimethyl-2-acetyl-7-ethylenedioxy-1,2,3,4,4aα,4b,5,6,7,8,-10,10aβ-dodecahydrophenanthrene-1,4-dione. Y: 96%. F. e. s. R. M. Lukes et al., Am. Soc. *75*, 1707 (1953).

Alkylation of ketones via α-hydroxymethyleneketones COCH → COCR

19.



2-Hydroxymethylene-6-methylcyclohexanone from 2-methylcyclohexanone methylated with excess methyl iodide-K-carbonate in boiling acetone for 12 hrs., the acetone distilled off, the residue treated with a large excess of aq. 20%-NaOH, then steam-distilled → 2,6-dimethylcyclohexanone. Y: 45%. F. E. and T. J. King, Soc. *1954*, 1373.

Alkylation of α-cyanocarboxylic acid esters ·HC(CN)COOR → ·R′C(CN)COOR
s. *6*, 802

Sodium acetate *CH_3COONa*

5-Substitution of barbituric acids ←
s. *7*, 834

Sodium cyanide *NaCN*

Replacement of halogen by cyano groups Hal → CN
s. *9*, 890

Pseudocyanides ←
s. *7*, 835

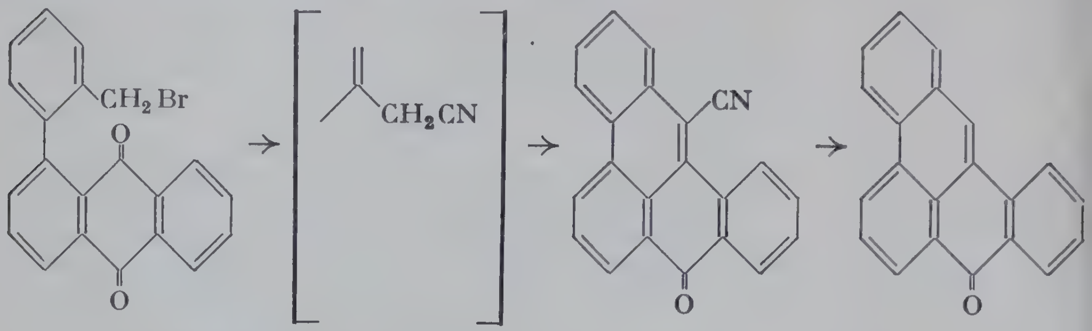
Potassium cyanide *KCN*

Nitriles from chlorides Cl → CN
s. *6*, 803

Carboxylic acids from halides Hal → COOH
Labeled compounds s. *9*, 891

Ring closure to isocyclics ←
with preceding replacement of bromine by cyano groups
Replacement of cyano groups by hydrogen

620.

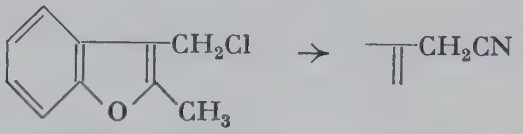


A mixture of 2 g. 1-o-bromomethylphenylanthraquinone, KCN, dioxane, and water refluxed 18 hrs. → 1.6 g. 4′-cyanonaphth(1′,2′,3′;1,13,9)-anthrone, 1 g. heated 4 hrs. at 160° with KOH and ethylene glycol → 0.8 g. *meso-α*-naphthanthrone. F. e. s. E. A. Braude, J. S. Fawcett, and A. A. Webb, Soc. *1954*, 1049.

Potassium cyanide and potassium iodide *KCN and KI*
s. Potassium iodide and potassium cyanide

Alkali iodide ←
Nitriles from chlorides Cl → CN

621.



A mixture of 3-(chloromethyl)-2-methylbenzofuran, powdered KCN, and 5%-soln. of KI in acetone refluxed with stirring → 2-methyl-3-benzofurylacetonitrile. Y: 75%. R. Gaertner, Am. Soc. *74*, 5319 (1952); with NaI s. Am. Soc. *74*, 2185.

Sodium iodide/sodium compound ←
Synthesis of γ-diketones from β-ketocarboxylic acid esters ←
via β,γ′-diketocarboxylic acid esters
Furans from β-diketones
s. *9*, 892

Potassium iodide and potassium cyanide *KI and KCN*
Stepwise replacement of chlorine by cyano groups Cl → CN
s. *8*, 853

Potassium iodide/potassium hydroxide *KI/KOH*
Alkylation of β-diketones CO·CH·CO → CO·CR·CO
s. *9*, 893

Choline *HOCH₂CH₂N(CH₃)₃OH*
Ethylene derivatives from halides by dimerization 2 >CHHal → >C:C<
s. *9*, 894

Triethylamine $(C_2H_5)_3N$

Ketene dimers from carboxylic acid chlorides ←
s. *7*, 862

Azetidinones ○
s. *7*, 836; penicilline ring system s. *9*, 895

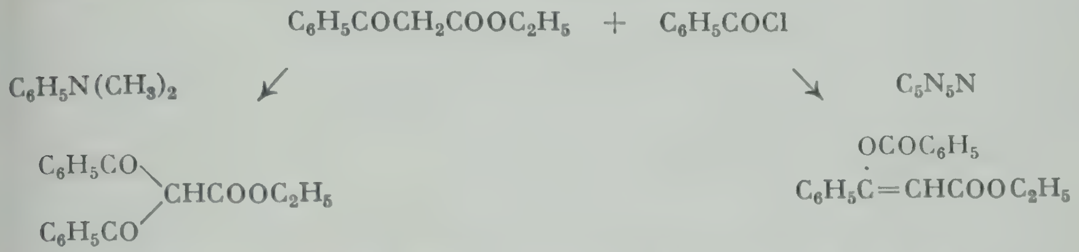
Piperidine $C_5H_{11}N$

3-Acyl-4-hydroxycoumarins from 4-hydroxycoumarins COCl → COR
s. *7*, 837

Dimethylaniline $C_6H_5N(CH_3)_2$

C- and O-Acylation of β-ketocarboxylic acid esters ←

2.



Benzoyl chloride added dropwise with stirring during

45 min. to a mixture of dimethylaniline and ethyl benzoylacetate, allowed to stand 24 hrs. at room temp. with occasional stirring → ethyl dibenzoylacetate. Y: 90.4%.

30 min. to a mixture of dry pyridine and ethyl benzoylacetate, the product isolated after 2 hrs.' stirring → ethyl (O-benzoyl)benzoylacetate. Y: 75.8%; Am. Soc. *64*, 254: 83%) and ethyl dibenzoylacetate (Y: 2.6%).

P. E. Wright and W. E. McEwen, Am. Soc. *76*, 4540 (1954); s. a. S. M. McElvain and D. M. Kundiger, Am. Soc. *64*, 254 (1942).

Pyridine C_5H_5N

Isoflavones ○
s. *9*, 896

Copper *Cu*

Diaryls from aryl halides ArHal+HalAr′ → Ar·Ar′
Sym. diaryls s. *8*, 888; *9*, 897; unsym. diaryls s. *8*, 854; with sand (s. a. *1*, 660) and anomalous reaction s. R. B. Carlin and E. A. Swakon, Am. Soc. 77, 966 (1955)

Introduction of carboxylic groups into ar. rings H → COOH
s. *6*, 763

Copper/potassium hydroxide *Cu/KOH*

Alkylation of β-diketones CO·CH·CO → CO·CR·CO
s. *9*, 893

Cupric acetate $(CH_3COO)_2Cu$

Pyran ring synthesis ○
s. *6*, 804

Cuprous cyanide *CuC*

Dimers from halides with simultaneous formation of a carbon-carbon double bond ←
s. *8*, 855

Rosenmund-von Braun nitrile synthesis Hal → C
s. *9*, 898

Carboxylic acids from halides Hal → COO
s. *8*, 856

α,β-Ethylenenitriles from ethylene derivatives via 1,2-dibromides and α-bromonitriles C:CH → C:C(CN
s. *9*, 899

Acylcyanides from carboxylic acid chlorides COCl → COC
s. *6*, 898

Cuprous halide/magnesium s. Magnesium/cuprous halide *CuHal/M*
Copper salt/lithium s. Lithium/copper salt ←

Silver perchlorate *AgClO*

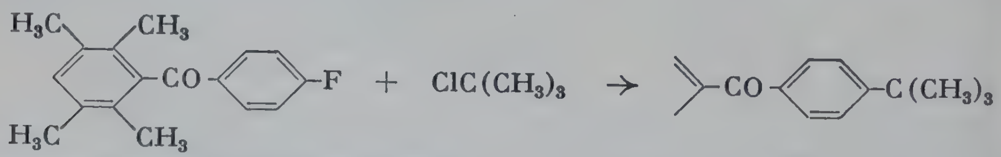
Ketones from carboxylic acid chlorides COCl → CO
s. *7*, 838

Silver bromide/magnesium s. Magnesium/silver bromide *AgBr/M*

Magnesium *M*

Synthesis of hydrocarbons from halides RHal+HalR′ → R·F
s. *8*, 857

623.



Reactions with hindered aryl ketones. An ethereal soln. of duryl p fluorophenyl ketone added to a soln. of *tert*-butyl-MgCl from *tert*-buty chloride and Mg in ether, and refluxed 15 hrs. → crude p-*tert*-butyl phenyl duryl ketone. Y: 84%. F. e. s. R. C. Fuson, W. S. Friedlander and G. W. Parshall, Am. Soc. *76*, 5119 (1954).

Ethylenesilanes
s. *9*, 900

3-Pyridyl compounds
s. *9*, 901

Selective replacement of chlorine
s. *6*, 806

Inverse addition of organometallic reagents
s. *9*, 878

Hydrocarbons from tert. amines R·N< → R·R
s. *6*, 805

Syntheses with quaternary ammonium salts ←
s. *7*, 840

α,ω-Addition to polyenes ←
s. *7*, 839

Synthesis of ethylene derivatives from enolethers ←
s. *8*, 858

Ethylene derivatives from aldehydes $CHO \rightarrow CH{:}CH$
$\alpha.\beta$-Ethyleneketones s. *6*, 807

Prim. alcohols from halides $Hal \rightarrow CH_2OH$
Synthesis with addition of 1 C-atom

24. $$[(CH_3)_3C\cdot Cl] \rightarrow (CH_3)_3C\cdot MgCl + HCOOCH_3 \rightarrow [(CH_3)_3C\cdot CHO]$$
$$\downarrow$$
$$(CH_3)_3C\cdot CH_2OH$$

13.5 moles of methyl formate added during 12 hrs. to 27 moles of *tert*-butyl-MgCl in ether, and stirring continued for 12 hrs. → neopentyl alcohol (startg. m. f. 446). Y: 72%. L. H. Sommer, H. D. Blankman, and P. C. Miller, Am. Soc. *76*, 803 (1954).

Sec. alcohols from carboxylic acid esters $COOR \rightarrow CH(OH)R'$
s. *7*, 841

Synthesis of ethers from acetals $CH(OR)_2 \rightarrow CH(OR)R'$
s. *9*, 902

Aldehydes from halides $Hal \rightarrow CHO$

via acetals
s. *9*, 903; s. a. R. P. Gandhi, V. S. Gaind, and S. M. Mukherji, Soc. *1955*, 2530

with N-phenylformimidate
s. *6*, 808

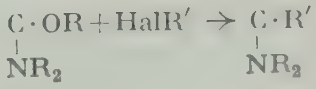
Ketones from carboxylic acid chlorides $COCl \rightarrow COR$
Steric hindrance in Grignard reactions
s. *6*, 809; s. a. M. Charpentier-Morize, Bl. *1954*, 497

Carboxylic acids from halides $Hal \rightarrow COOH$
Improved procedure and labeled compounds
s. *7*, 842; labeled compounds s. a. W. R. Vaughan and D. J. McCane, Am. Soc. *76*, 2504 (1954)

Ketocarboxylic acids from dicarboxylic acid anhydrides ←
s. *6*, 810

Alkylation of malonic esters $RCH(COOR)_2$
s. *7*, 843

Tert. amines from 1-aminoethers
s. *10*, 316


$$\underset{NR_2}{\underset{|}{C}}\cdot OR + HalR' \rightarrow \underset{NR_2}{\underset{|}{C}}\cdot R'$$

Synthesis of amines from carboxylic acid amides ←
Triply α-branched amines s. *7*, 844

Reactions of nitriles with Grignard reagents ○
Pseudoisoindoles s. *7*, 845

Magnesium/cuprous halide *Mg/CuHal*

1,4-Diynes from α,β-acetylenehalides Hal → C⋮CR
s. *7*, 846; s. a. Am. Soc. *77*, 3076 (1955)

Highly branched ketones from carboxylic acid chlorides COCl → COR
s. *6*, 811; also from carboxylic acid anhydrides s. M. F. Ansell et al., Soc. *1955*, 2705

Magnesium/silver bromide *Mg/AgBr*

Dimerization of halides 2 RHal → R·R
s. *7*, 847; *8*, 859

Magnesium/ethanol *Mg/C_2H_5OH*

C-Acylation C·H → C·COR
s. *9*, 904; s. a. D. G. Doherty, Am. Soc. *77*, 4887 (1955)

Magnesium/ethyl bromide *Mg/C_2H_5Br*

β-Subst. ethyl alcohols
Syntheses with ethylene oxide Hal → CH_2CH_2OH
s. *1*, 674; s. a. A. L. Green and D. H. Hey, Soc. *1954*, 4306

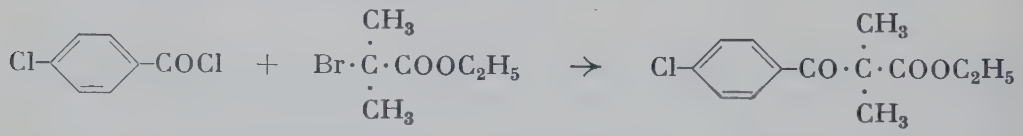
Magnesium/ferric chloride *$Mg/FeCl_3$*

Ketones from carboxylic acid chlorides COCl → COR
s. *4*, 783; silicon compounds s. L. H. Sommer and R. P. Pioch, Am. Soc. *76*, 1606 (1954)

Zinc *Zn*

β-Ketocarboxylic acid esters from carboxylic acid chlorides COCl → COC·COOR

625.



One quarter of a soln. of p-chlorobenzoyl chloride and ethyl α-bromoisobutyrate in anhydrous ether added to Zn-foil, stirred and warmed until reaction begins, then the remainder of the soln. added at a rate to maintain gentle refluxing, stirring and refluxing continued until after 2-3 hrs. practically all of the Zn has reacted → ethyl α-(p-chlorobenzoyl)isobutyrate. Y: 71%. F. e. s. P. L. Bayless and C. R. Hauser, Am. Soc. *76*, 2306 (1954).

5,6-Dihydro-2-pyrones ○
s. *7*, 848

Zinc/acetic anhydride *$Zn/(CH_3CO)_2O$*

Dimerization of halides 2 RHal → R·R
s. *9*, 905

Alkylmagnesium halide *RMgHal*

Synthesis of hydrocarbons from halides RH+HalR′ → R·R′
s. *9*, 906

Zinc chloride *$ZnCl_2$*

Ketones from carboxylic acid chlorides COCl → COR
s. *6*, 813; *10*, 103

Cadmium chloride *$CdCl_2$*

s. *7*, 849; ketocarboxylic acid esters s. R. Huisgen et al., A. *586*, 52 (1954)

Diketodicarboxylic acid esters from dihalides
s. *9*, 907

Mercuric iodide/lithium *HgI_2/Li*

Synthesis of acetylene derivatives via acetylenemercury compounds ←
s. *8*, 870

Aluminum *Al*

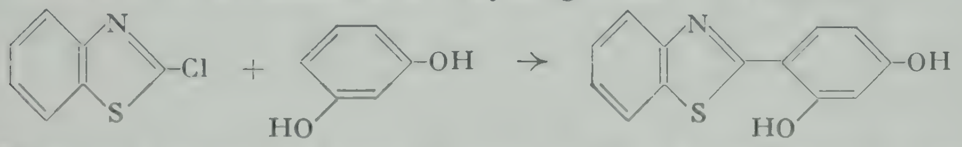
Ketones from carboxylic acid chlorides COCl → COR
s. *7*, 850

Aluminum/hydrochloric acid *Al/HCl*

Synthesis of hydrocarbons from halides according to Radzivanovskiĭ ArH → ArR
s. *7*, 851

Aluminum chloride *$AlCl_3$*

Condensation with elimination of hydrogen chloride RCl+HR′ → R·R′



$AlCl_3$ added gradually during 15 min. at 15° to a well-stirred soln. of resorcinol and 2-chlorobenzothiazole in *quinoline*, the inside temp. raised to 150° within 0.5 hr. and maintained 10 hrs. at this level → 2-(2.4-dihydroxyphenyl)benzothiazole. Y: 43-59%. F. e., with lower yields. s. G. Illuminati and H. Gilman, Am. Soc. *74*, 2896 (1952).

Friedel-Crafts ketone syntheses RH → RCOR′

$$FCH_2COCl + C_6H_6 \rightarrow FCH_2COC_6H_5$$

ω-Fluoroacetophenone (startg. m. f. 520) can be obtained in 81% yield by the Friedel-Crafts method, if the reaction with fluoroacetyl chloride is carried out rapidly in a homogeneous medium, e.g. methylene chloride. By this procedure the formation of the chloro analog by halogen exchange is avoided. F. Bergmann and A. Kalmus, Am. Soc. *76*, 4137 (1954).

s. a. *7*, 852; *8*, 860; *9*, 908; 2,3a-diazaindene derivatives s. J. D. Bower and G. R. Ramage, Soc. *1955*, 2834

$$C_6H_6 + ClCOCH_3 \rightarrow C_6H_5COCH_3$$

Improved procedure. Elimination of HCl by a continuous passage of a stream of dry air gives high yields in reaction times of near 0.5 hr. and usually under mild temp. conditions with no by-product formation.—E: Benzene and acetyl chloride at 15-20° → acetophenone. Y 97%. Recommended temp. for other compounds s. F. Smeets and J. Verhulst, Bl. Soc. chim. Belg. *61*, 694 (1952).

Perrier procedure
s. *2*, 748; *3*, 697; modified procedure for the characterization of ar. hydrocarbons s. H. Pines and A. W. Shaw, J. Org. Chem. *20*, 373 (1955)

Formation of cyclic ketones as by-products
s. *8*, 861

Orientation in the acylation of naphthalene
s. *5*, 604; s. a. H. F. Bassilios, S. M. Makar, and A. Y. Salem, Bl. *1954*, 72.

Vinylketones
s. *6*, 814; s. a. L. J. Reed and C.-I. Niu, Am. Soc. *77*, 416 (1955)

Alkoxyketones by a modified procedure
s. *7*, 853; cf. H. Wolkowitz and M. Dunn, Biochem. Prep. *4*, 6 (1955)

Acylaminoketones
with acylaminoarenes s. *5*, 605; with acylamino carboxylic acid chlorides s. K. Heyns and W. Pyrus, B. *88*, 678 (1955)

Ketothioethers
s. *9*, 909

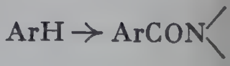
Improved Zincke-Suhl synthesis of cyclohexadienones ←

Synthesis of ketones from 1,1,1-trichlorides
s. *9*, 910

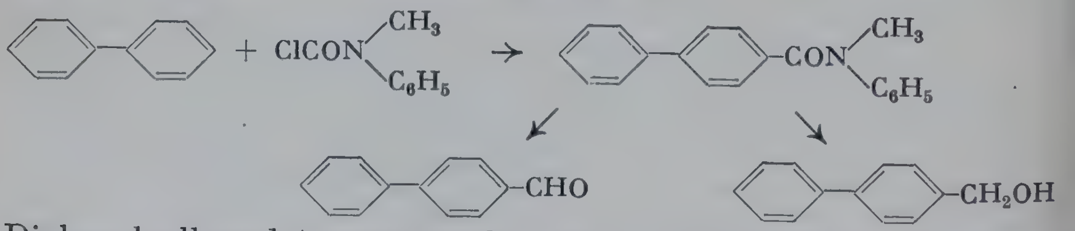
1,2-Diaroylethylenes COCH:CHCO
s. *6*, 815

α-Ketocarboxylic acids COCOOH
s. *6*, 817

Introduction of aldehyde and hydroxymethyl groups into ar. rings via carboxylic acid amides


$ArH \rightarrow ArCON$

629.



Diphenyl allowed to react with 1 mole N-methyl-N-phenylcarbamyl chloride (prepn. s. 354) and $AlCl_3$ at 110-120° for 3 hrs. → 4-phenylbenzoyl-N-methylanilide (Y: 38.5%) allowed to react in tetrahydrofuran with

0.5 mole $LiAlH_4$ at 0° for 8 hrs. → 4-phenylbenzaldehyde (Y: 70% as the 2,4-dinitrophenylhydrazone).

excess $LiAlH_4$ at reflux temp. for 4 hrs. → 4-phenylbenzyl alcohol (Y: 75%).

F. e. s. F. Weygand and R. Mitgau, B. *88*, 301 (1955).

Ketones from iminohalides via azomethines $C(:NH)Cl \rightarrow COR$
s. *7*, 854

Sym. benzophenones RCOR
s. *6*, 816

Sym. β-diketones from carboxylic acid chlorides ←
s. *8*, 862

Synthesis of phthalides from ketocarboxylic acids via halogenophthalides ←
s. *7*, 855

Thianaphthenequinones ○
s. *6*, 818

Thiaxanthylium salts
s. *8*, 863

Aluminum chloride/sulfuric acid $AlCl_3/H_2SO_4$

One-step indanone ring synthesis
s. *6*, 819

Aluminum bromide $AlBr_3$

Synthesis of hydrocarbons from bromides $CBr \rightarrow CR$
s. *9*, 911

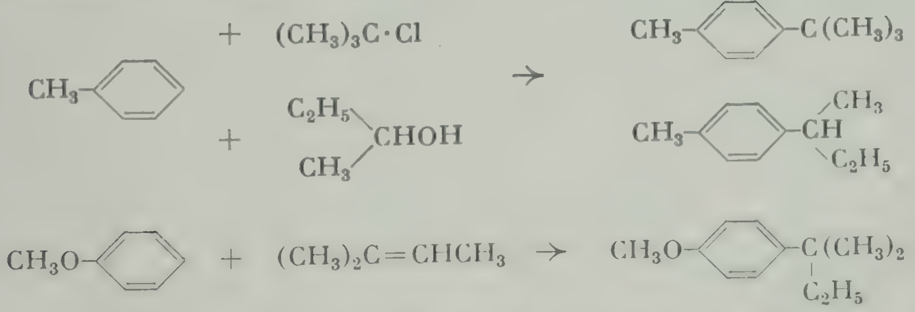
Friedel-Crafts ketone syntheses $RH \rightarrow RCOR'$
Ketomercaptans s. *9*, 655

Acetic acid CH_3COOH

3-Halogenoquinolines ○
s. *7*, 762; s. a. S. W. Tinsley, Am. Soc. 77, 4175 (1955)

Titanium tetrachloride $TiCl_4$

in the Friedel-Crafts reaction
C-Alkylation $CH \rightarrow CR$
with halides, alcohols, and ethylene derivatives



While $TiCl_4$ is not as active as $AlCl_3$, it has certain advantages: owing to its solubility in organic solvents reactions can be carried out in homogeneous media, and solvents such as CS_2 can be dispensed with. Noteworthy is the absence of much polyalkylation. All disubst. products are *para* only.—With alkyl halides small proportions of $TiCl_4$ suffice, but with the alcohols at least an equivalent is required.—Isobutyl alcohol tends to yield *tert*-butyl derivatives.–E: $TiCl_4$ added at 10° with agitation and cooling to toluene and *tert*-butyl chloride, and the product isolated after 1 hr. → p-*tert*-butyltoluene. Y: 77%.—Similarly:

Toluene and *sec*-butanol allowed to react at 60° during 3 hrs. → p-*sec*-butyltoluene. Y: 74%.—Anisole and 2-methyl-2-butene at 20° during 0.25 hr. → p-*tert*-amylanisole. Y: 67%. F. e. s. N. M. Cullinane and D. M. Leyshon, Soc. *1954*, 2942.

Stannic chloride *$SnCl_4$*

Ketones from carboxylic acid chlorides COCl → COR

s. *2*, 751; thiophene derivatives s. G. M. Badger, H. J. Rodda, and W. H. F. Sasse, Soc. *1954*, 4162

Shortened phenanthridine ring closure ○
6-Alkoxy-5,6-dihydrophenanthridines
from phenanthridinium salts

s. *6*, 820

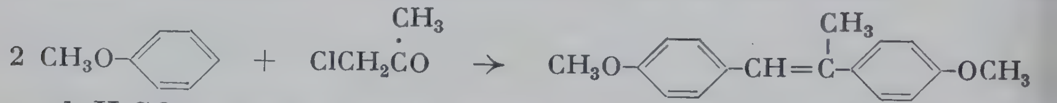
Sulfuric acid *H_2SO_4*

Condensation with elimination of hydrogen chloride RCl+HR′ → R·R′

s. *8*, 864

Synthesis of ethylene derivatives from α-halogenoketones ←

631.



Concd. H_2SO_4 added dropwise at 0° during 0.5 hr. to a stirred mixture of anisole and chloroacetone, stirring continued for 4-5 hrs. → 4,4′-dimethoxy-α-methylstilbene. Y: 77.5%. F. e., also with phenol, s. S. H. Zaheer et al., Soc. *1954*, 3360.

Chromium sulfate *$CrSO_4$*

Dimerization 2 RHal → R·R

s. *6*, 821

Ferric oxide *Fe_2O_3*

Condensation with elimination of hydrogen chloride RCl+HR′ → R·R′

s. *7*, 856

Ferric chloride *$FeCl_3$*

Alkylation of arenes ArH+ClR → ArR

s. *8*, 865

Ferric bromide *$FeBr_3$*

Dimerization 2 RHal → R·R

Dipyridyls s. *6*, 822

Nickel carbonyl *$Ni(CO)_4$*

Dimerization of α,β-ethylenehalides ←

s. *8*, 866

Via intermediates *v.i.*

Substitution of ketones via enamines COCH → COCR

s. *9*, 912

β,γ-Ethylenenitriles from β,γ-ethylenehalides ←
via malonic esters and α-oximinocarboxylic acids

s. *6*, 823

Sulfur ↓

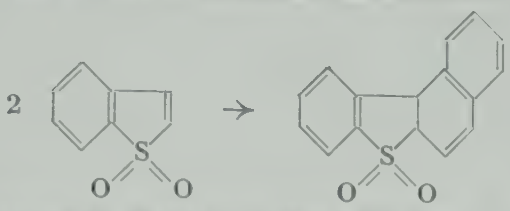
CC⇅S

Without additional reagents

w.a.r.

9-Thiafluorenes from 2 thianaphthene molecules ←

32.



Thianaphthene dioxide in tetralin heated 90 min. at 180-182° in a bath of boiling aniline → 10,11-dihydro-9-thia-3,4-benzofluorene 9,9-dioxide (startg. m. f. 691). Y: 88%. W. Davies, N. W. Gamble and W. E. Savige, Soc. *1952*, 4678.

Lithium/mercuric iodide s. Mercuric iodide/lithium *Li/HgI$_2$*

Potassium hydroxide *KOH*

Bianthronyls ←
s. *8*, 867

Sodium carbonate *Na$_2$CO$_3$*

α-Alkylsulfones via thiophene 1,1-dioxides ←
s. *8*, 868

Sodium cyanide *NaCN*

Nitriles from sulfuric acid esters ←
Labeled compounds s. *8*, 869

Zinc chloride/acetic anhydride *ZnCl$_2$/(CH$_3$CO)$_2$O*

Alkylthiomethylene compounds from orthotrithioformic acid esters C:CHSR
s. *9*, 913

Mercuric iodide/lithium *HgI$_2$/Li*

Synthesis of acetylene derivatives via acetylenemercury compounds ←
s. *8*, 870

Basic lead carbonate *Pb(OH)$_2$·PbCO$_3$*

Cyanoformamidines from thioureas ←
Labeled compounds s. *6*, 824

Remaining Elements ↓

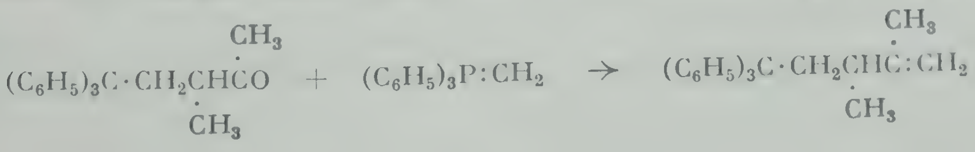
CC⇅Rem

Without additional reagents

w.a.r.

Synthesis of ethylene derivatives from alkylidenephosphines and oxo compounds ←

$C_6H_5CHO + (C_6H_5)_3P:CHCH:CH_2 \rightarrow C_6H_5CH:CHCH:CH_2 + (C_6H_5)_3PO$



$$(C_6H_5)_3C\cdot CH_2\overset{CH_3}{\underset{CH_3}{C}}HCO + (C_6H_5)_3P:CH_2 \rightarrow (C_6H_5)_3C\cdot CH_2CH\overset{CH_3}{\underset{CH_3}{C}}:CH_2$$

Wittig reaction. Benzaldehyde added to a suspension of triphenylphosphine vinylmethylene in ether, shaken 2 hrs., and heated 2 hrs. a 60-70° → 1-phenylbutadiene (Y: 58%) and triphenylphosphine oxid (Y: 92%).—Similarly with 3-methyl-1,1,1-triphenyl-4-pentanone and triphenylphosphine methylene → 3,4-dimethyl-1,1,1-triphenyl-4-pentene. Y: 71%.—This method has the advantage that, contrary to the Saytzeff rule, the carbon-carbon double bond is formed without shif at the place of the original carbon-oxygen double bond. F. e. s. G. Wittig, U. Schöllkopf, and W. Haag, B. *87*, 1318 (1954); *88*, 1654 (1955); s. a. F. Bohlmann et al., B. 88, 1330, 1347 (1955); H. H. Inhoffen et al., B. *88*, 1415 (1955); cf. I. T. Harrison, B. Lythgoe, and S. Trippett, Soc. *1955*, 4016.

Ketones from organocobalt compounds ←
s. *8*, 871

Lithium *Li*

Synthesis of acetylene derivatives via acetylenemercury compounds ←
s. *8*, 870

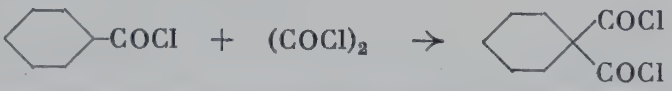
Carbon ↑ CC⇅C

Without additional reagents *w.a.r.*

Alkylation of p-quinones with acyl peroxides H → R
s. *3*, 701; quinolinequinones cf. Y. T. Pratt and N. L. Drake, Am. Soc. *77*, 4664 (1955)

α-Dicarboxylic acid chlorides from carboxylic acid chlorides H → COCl

634.



Cyclohexanecarboxylic acid chloride boiled 10 hrs. with oxalyl chloride → cyclohexane-1,1-dicarboxylic acid chloride (startg. m. f. 358). Y: 82.5%. F. e. s. G. Kühnhanss and J. Teubel, J. pr. *1*, 87 (1955).

Allyl-aminomethane derivatives ←
s. *6*, 825

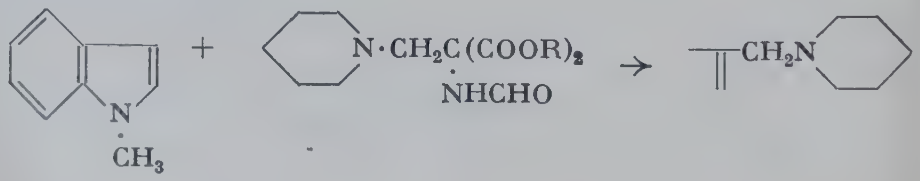
Diene synthesis – Benzene ring from cyclones ←
s. *7*, 857

Sodium oxide/chromium oxide s. Chromium oxide/sodium oxide *Na_2O/Cr_2O_3*

Sodium hydroxide *NaOH*

Transaminomethylation ←

635.



N-Methylindole, ethyl (piperidinomethyl)formamidomalonate, and powdered NaOH in anhydrous xylene refluxed 4 hrs. → 1-methyl-3-piperidinomethylindole. Y: 70%. H. Hellmann and F. Lingens, B. 87, 940 (1954).

α,β-Ethylene-γ-diketones and cyclopentenones ←
from α-ketoaldehydes and β-ketocarboxylic acids
via α-hydroxy-γ-diketones
s. *6*, 826

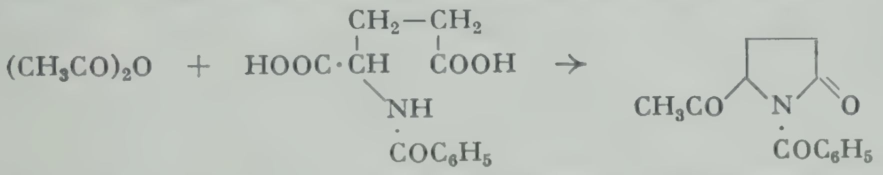
Phenyllithium *C_6H_5Li*

1-β-Acylethylisoquinolines from ←
2-acyl-1,2-dihydroisoquinaldo-1-nitriles (Reissert compounds)
via 7,8-benzindolizines
s. *8*, 872

Pyridine *C_5H_5N*

Ketones, also sym., from carboxylic acid anhydrides ←
Selfcondensation of carboxylic acid anhydrides
Decarboxylative acylation
s. *9*, 914; s. a. Am. Soc. *77*, 2814 (1955)

2-Pyrrolidone ring closure with decarboxylative acylation ○



Benzoyl-DL-glutamic acid, anhydrous pyridine, and acetic anhydride heated 45 min. at 110° → 5-acetyl-1-benzoyl-2-pyrrolidone. Y: 90%. F. e. s. R. A. F. Bullerwell, A. Lawson, and H. V. Morley, Soc. *1954*, 3283.

Silver salt *Ag^+*

Hydrocarbons from carboxylic acids by dimerization ←
s. *8*, 873

Calcium hydroxide *$Ca(OH)_2$*

Synthesis with addition of 1 C-atom via enolbetaines ←
s. *7*, 859

Magnesium *Mg*

Synthesis of amines from α-aminonitriles C·CN → C·R
s. *7*, 858

2-Quinolylcarbinols from ←
1-acyl-1,2-dihydroquinaldo-2-nitriles (Reissert compounds)
s. *8*, 874

Magnesium oxide *MgO*

Sym. ketones from 2 carboxylic acid molecules 2 RCOOH → RCOR
s. *9*, 915

Zinc/acetic acid *Zn/CH_3COOH*

Reductive ring closure ○
Pyrrole ring synthesis s. *7*, 860

Boron fluoride *BF_3*

Sym. ketones from carboxylic acid anhydrides RCO·O·OCR → RCOR
Selfcondensation of carboxylic acid anhydrides
s. *6*, 827

Aluminum chloride *$AlCl_3$*

Synthesis of hydrocarbons from ethylene derivatives with exchange of C-aryl groups ←
s. *8*, 875

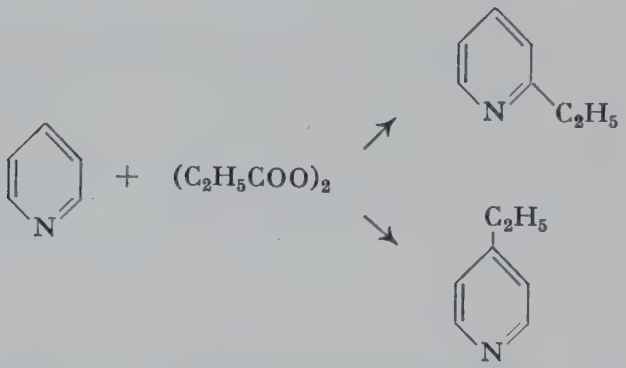
Synthesis of hydrocarbons from carboxylic acid chlorides and of carboxylic acids from carboxylic acid anhydrides ←
s. *6*, 828

Aminoketones from N-carboxyaminocarboxylic acid anhydrides ←
s. *6*, 829

Carboxylic acids *RCOOH*

Syntheses with acyl peroxides
C-Alkylation of N-heterocyclics ArH → ArR

637.



27.3 g. dipropionyl peroxide in anhydrous propionic acid added dropwise to pyridine during 45 min. at 100° → 11.8 g. 2-ethylpyridine and 5.5 g. 4-ethylpyridine. Total Y: 86.5%. F. e. s. S. Goldschmidt and M. Minsinger, B. *87*, 956 (1954).

Acetic acid *CH_3COOH*

Methylene condensation ←
s. *6*, 830

Exchange reactions of polyhydroxydiarylmethanes ←
Rottlerone change
s. *8*, 876

Lead oxide *PbO*

Decarboxylative condensation ←
Synthesis of polyenes s. *8*, 877

Sulfuric acid *H_2SO_4*

2-Pyrones ○
s. *7*, 861

Chromium oxide/sodium oxide *Cr_2O_3/Na_2O*

Ketones from 2 aldehyde molecules ←

cf. Synth. Meth. *1*, 718
The optimum Na-content of the chromia catalyst is ca. 1.0%. J. R. Coley and V. I. Komarevsky, Am. Soc. *74*, 4448 (1952).

Hydrochloric acid *HCl*

Synthesis of porphyrins ○
s. *6*, 831

Via intermediates *v.i.*

Sym. ketones from carboxylic acid chlorides via ketene dimers $2\,\mathrm{RCOCl} \rightarrow \mathrm{RCOR}$
s. *7*, 862

Acetylenedicarboxylic acid ester synthesis ←
Alder-Rickert synthesis

Valence tautomerism
s. *9*, 917

Furan derivatives
s. *3*, 704; hydrogenation with Pd-$CaCO_3$ s. H. Williams, P. Kaufmann, and H. S. Mosher, J. Org. Chem. *20*, 1139 (1955)

Elimination

Hydrogen ↑ CC ⇑ H

Without additional reagents *w.a.r.*

Pyridazine ring closure ○
s. *6*, 832

Irradiation

Ring closure
isocyclics s. *7*, 863; N-heterocyclics s. D. Jerchel et al., B. *88*, 1284, 1595 (1955)

Calcined magnesite *MgO*

α,β-Ethylenearenes by dehydrogenation $\mathrm{CHCH} \rightarrow \mathrm{C{:}C}$
s. *9*, 918

Zinc oxide-alumina-calcium oxide *ZnO, Al_2O_3, CaO*

Dehydrogenation in the vapor phase
s. *9*, 919

Mercuric acetate $(CH_3COO)_2H$

Dienes from ethylene derivatives
s. *7*, 864; s. a. Helv. *37*, 250 (1954)

Aluminum chloride/hydrochloric acid $AlCl_3/HC$

Scholl ring closure – Migration of alkyl groups
s. *6*, 833

α,β-Ethyleneketones   *C:C·C*

Pyrimidines from dihydropyrimidines   ←
s. *8*, 454

Quinones   ←

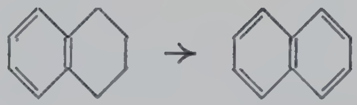
Bianthrones from bianthronyls   CHCH → C:
s. *9*, 920

Chloranil   ←

Dehydrogenation
s. *9*, 921; *10*, 667

Dichlorodicyanoquinone   ←

639.

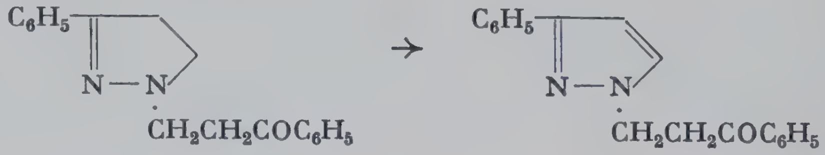


Among 11 quinones tested, the most effective was 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. It converts tetralin into naphthalene in practically quantitative yield in boiling benzene during 2 hrs. F. e. s. E. A Braude, A. G. Brook, and R. P. Linstead, Soc. *1954*, 3569.

Lead dioxide PbO_2

Pyrazoles from pyrazolines

640.



90%-PbO_2 added in small portions during 15 min. to a soln. of 1-(β-benzoylethyl)-3-phenyl-Δ^2-pyrazoline (prepn. s. 344) in glacial acetic acid heated on a steam bath → 1-(β-benzoylethyl)-3-phenylpyrazole. Y: 66%. F. e. s. M. Stamper and B. F. Aycock, Am. Soc. *76*, 2786 (1954).

Phosphorus oxychloride $POCl_3$

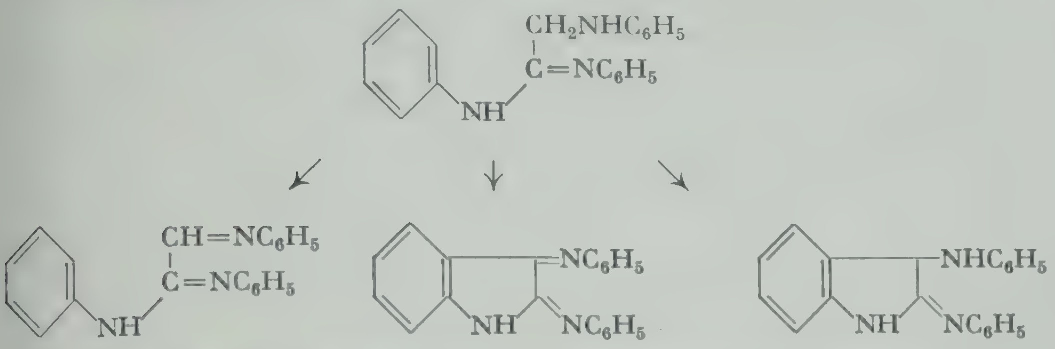
Bischler-Napieralski ring closure with simultaneous oxidation
s. *6*, 834; cf. C. F. Huebner, H. A. Troxell, and D. C. Schroeder, Am. Soc. *75*, 5887 (1953)

Oxygen

O_2

←

Glyoxylamidine anils, 3-amino-2-iminoindolines, and isatindianils from Sabaneyev bases



A soln. of N-phenylglycine N,N′-diphenylamidine

in chlorobenzene		in decalin
warmed 2 hrs. at 60-65° → glyoxyl-N,N′-diphenylamidine anil. Y: 67%.	stirred and treated 3 hrs. with O_2 → isatin dianil. Y: 30-35%.	stirred and treated 2 hrs. with O_2 → 2-phenylimino-3-phenylaminodihydroindole. Y: 50%.

F. e. s. E. Ziegler, W. Kaufmann, and W. Klementschitz, M. *83*, 1334 (1952).

S

Sulfur

CHCH → C:C

Aromatization

s. *6*, 858; *8*, 946; *9*, 923

←

Ar. hydrocarbons from cyclic alcohols

s. *7*, 885

Se

Selenium

←

Aromatization – N-Heterocyclics

s. *8*, 561

SeO_2

Selenium dioxide

CHCH → C:C

Dehydrogenation

s. *7*, 865

Ene-1,4-diones from 1,4-diketones

s. *9*, 922

Cr-Cu-C

Chromium-copper-carbon

s. *8*, 544

CrO_3

Chromic acid

s. *6*, 709; 9(H)-Pyrid[3,4-b]indoles s. *6*, 780

Cl

Chlorine

○

Halogenoisocyclics

s. *8*, 878

Bromine *Br*

Dehydrogenation of (o-di-N)-heterocyclics CHCH → C:C
s. *6*, 835; *7*, 866

Aromatization
s. *3*, 579; s. a. E. R. Ward and T. M. Coulson, Soc. *1954*, 4545

Stepwise aromatization
Phenanthrene derivatives s. *9*, 923

Tropolones from α-diketones ←
s. *8*, 879

Cobalt-silica *Co-SiO*$_2$

Dehydrogenation CHCH → C:C
s. *6*, 836

Nickel-copper-chromium-platinum/sodium sulfate *Ni,Cu,Cr,Pt/Na*$_2$*SO*$_4$

Phenols by dehydrogenation
s. *8*, 880

Palladium-barium sulfate *Pd-BaSO*$_4$
s. *7*, 867

Palladium-carbon *Pd-C*
s. *8*, 946; *9*, 859, 931; s. a. W. J. Bailey and Chien-Wei Liao, Am. Soc. *77*, 992 (1955)

in the vapor phase
s. *6*, 837; s. a. E. Kováts, P. A. Plattner, and H. H. Günthard, Helv. *37*, 983 (1954)

Dehydrogenation and epimerization ←
The action of palladium-on-charcoal catalyst on steroids
s. *6*, 838

Palladium-carbon/magnesium oxide *Pd-C/MgO*

Dehydrogenation CHCH → C:C
s. *9*, 924

Palladium-pumice
s. *6*, 839 ←

Palladium,platinum-carbon *Pd,Pt-C*
s. *9*, 925/6

Via intermediates *v.i.*

Dehydrogenation via bromides
s. *6*, 840; *10*, 680; also β,γ-ethylenebromides from hydrocarbons s. *9*, 927

Dienes from ethylene derivatives via 1,2-dibromides
s. *9*, 928

Oxygen ↑ CC ⇑ O

Without additional reagents *w.a.r.*

Thermal cleavage of carboxylic acid esters

Ethylene derivatives from acetates CHC(OAc) → C:C

2. cf. Synth. Meth. *2*, 768; *4*, 814

When unsym. sec. esters are pyrolyzed under mild conditions only the olefin having the smallest number of attached alkyl groups is formed following the Hofmann rule. E. s. W. J. Bailey and C. King, Am. Soc. *77*, 75 (1955).

Exocyclic carbon-carbon double bonds s. Am. Soc. *77*, 73 (1955).

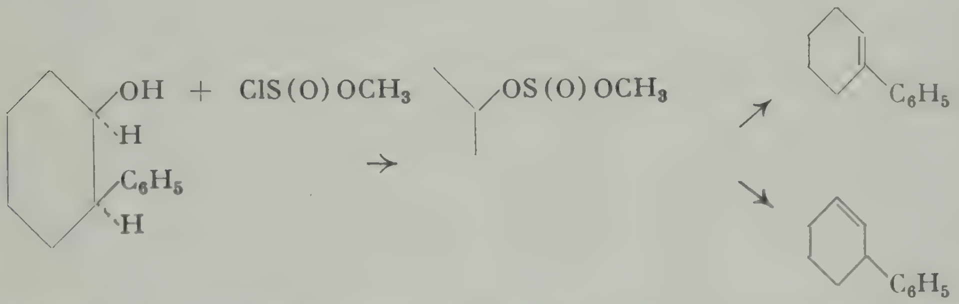
Styrenes s. C. G. Overberger and D. Tanner, Am. Soc. *77*, 369 (1955).

Dehydration of alcohols CHC(OH) → C:C

via carbonic acid esters

s. *8*, 915

3.



via mixed sulfurous acid esters. A soln. of methyl chlorosulfinate in dry ether added slowly at −5° with stirring to a soln. of *cis*-2-phenylcyclohexanol and pyridine in ether, and stirring continued for 30 min. → methyl *cis*-2-phenylcyclohexyl sulfite (Crude Y: 95%; pure Y: 80%; dioxane and benzene as solvents gave equally good results.) pyrolyzed and distilled under N_2 at 170-270° → 93% yield of mixture of 70% 1-phenylcyclohexene and 30% 3-phenyl isomer from crude sulfite or 97% yield of mixture of 78% 1-phenyl and 22% 3-phenyl isomer from pure sulfite.—The yields are usually higher than in the Chugaev reaction, but the method lacks in stereospecificity. The pyrolysis temp., although higher than those of te corresponding xanthates, are much lower than those of the acetates. F. e. s. G. Berti, Am. Soc. *76*, 1213 (1954).

via xanthates – Chugaev reaction

cis-Elimination s. *6*, 841; trans-elimination, also with acetates, s. A. T. Blomquist and A. Goldstein, Am. Soc. *77*, 1001 (1955)

***α,β*-Ethylenenitriles from cyanohydrin acetates** CHC(OAc) → C:C

s. *8*, 717

Ethylene derivatives from acoxy compounds with simultaneous ether cleavage

1,3,5-Triazine derivatives s. *8*, 881

Enolethers from acetals $CHC(OR)_2 \rightarrow C{:}C(OR)$
s. *9*, 929

Hydroxyindoles ○
s. *9*, 930

1-Cyclopentenealdehydes – Ring contraction ←
s. *6*, 842

Sodium *Na*

Acyloin condensation ┌CH(OH) CO┐
Paracyclophanes s. *9*, 931

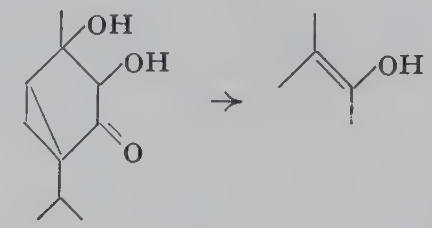
Sodium hydride *NaH*

Dieckmann cyclization ○
Cyclic β-diketones s. *8*, 885

Sodium hydroxide *NaOH*

Dehydration CHC(OH) → C:C

644.



Enols from glycols. 1,2-Dihydroxydihydroumbellulone refluxed 5 min. in aq. 1%-NaOH → α-hydroxyumbellulone. Y: 60%. R. H. Eastman and J. C. Selover, Am. Soc. *76*, 4118 (1954).

with simultaneous formation of
carboxylic acids from 1,1,1-trihalides
s. *7*, 868

Cyclopentenones from α-ketoaldehydes ○
and β-ketocarboxylic acids via α-hydroxy-β-diketones
s. *6*, 826

Cyclohexenone ring from ketones
via α-hydroxymethyleneketones and diketones
Modified Robinston-Mannich base procedure
Tert. amines as intermediates
s. *7*, 869

Phenol ring and pyrylium salts from diketones
s. *8*, 882

Anthrapyridones
s. *6*, 859

Sodium hydroxide/calcium oxide *NaOH/CaO*
s. Calcium oxide/sodium hydroxide

Potassium hydroxide *KOH*

Partial dehydration CHC(OH) → C:C
s. *9*, 239

Dehydration of ketones ←
s. *7*, 870

Ethylene derivatives from acoxy compounds CHC(OAc) → C:C
s. *7*, 774

Elimination reaction of esters ←
α,β-Ethylene- from β-acoxy-carboxylic acid esters
s. *9*, 932

Ethylene derivatives from sulfonic acid esters ←
Hydrolytic ring opening of isocyclics
s. *9*, 772

Ethylene derivatives from tosylates CHC(OTs) → C:C
s. *7*, 871

Ethylene derivatives and hydroxy compounds from sulfuric acid esters ←
s. *8*, 883

Cycloalkenone ring from diketones ○
with simultaneous decarbalkoxylation
s. *9*, 933

Cyclohexenone ring with simultaneous deformylation
s. *7*, 872

1-Cyclopentenealdehydes – Ring contraction ←
s. *7*, 873

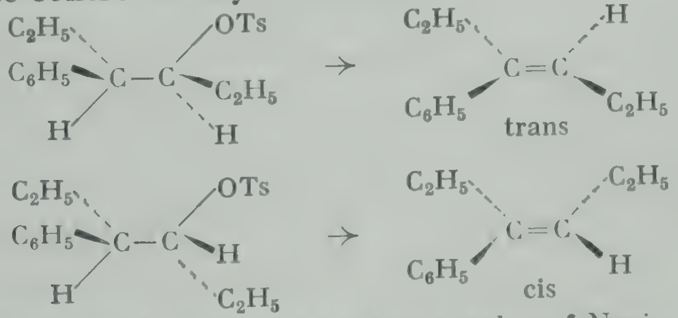
Potassium hydroxide/alcohol

Cyclohexenones ○
s. *6*, 843

Cyclohexenone ring from enollactones via enollactols
Labeling of steroids in the 4-position
s. *8*, 884

Sodium/alcohol *NaOR*

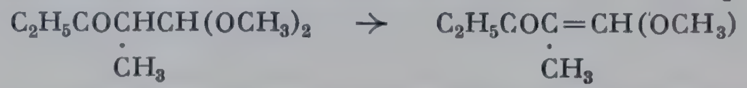
Ethylene derivatives from p-toluenesulfonic acid esters ←
trans-Elimination – Assignment of configuration
Rule of steric control of asym. induction



threo-4-Phenyl-3-hexyl tosylate added to a soln. of Na in abs. ethanol, and refluxed 14 hrs. → crude *trans*-3-phenyl-3-hexene. Y: 85%.—The *cis*-isomer is obtained from the *erythro*-isomer in the same way and with the same yield. Also "Rule of Steric Control of Asym. Induction" s. D. J. Cram, F. A. Abd Elhafez, and H. Weingartner, Am. Soc. *75*, 2293 (1953).

α-Alkoxymethyleneketones from β-ketoacetals $CHC(OR)_2 \rightarrow C{:}C(OR)$

646.



$$C_2H_5CO\underset{CH_3}{C}HCH(OCH_3)_2 \rightarrow C_2H_5CO\underset{CH_3}{C}{=}CH(OCH_3)$$

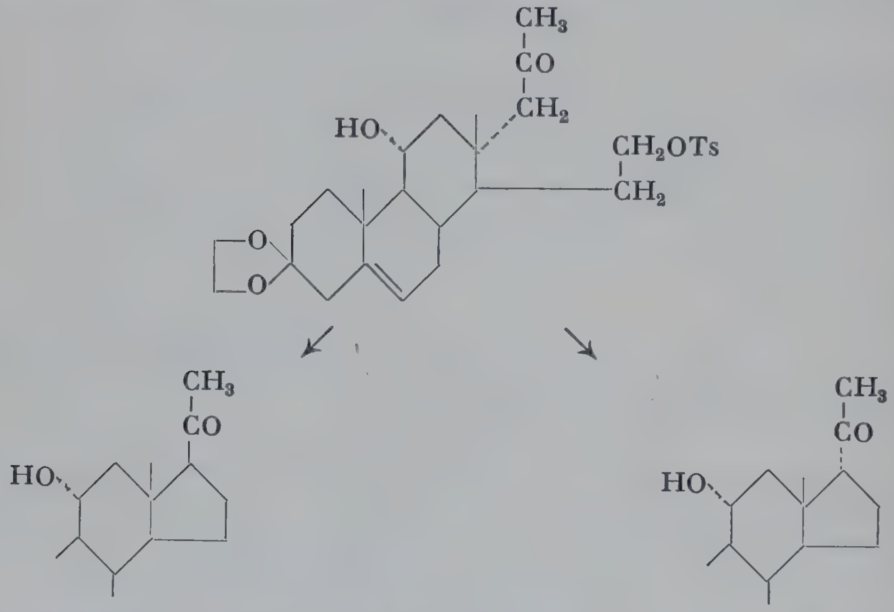
A soln. of 1,1-dimethoxy-2-methyl-3-pentanone dissolved in methanol, 1-2% by weight of solid Na-methoxide added, methanol then removed by distillation at ca. 150 mm. until the pot temp. reaches 60-75°, the pressure reduced slowly maintaining the same temp. range, and distilled in vacuo after removal of the methanol → 2-methoxymethylene-3-pentanone. Y: 76.4%. F. e. s. E. E. Royals and K. C. Brannock, Am. Soc. *76*, 3041 (1954).

Dieckmann cyclization ○

Cyclic β-diketones s. *8*, 885

Isocyclics from p-toluenesulfonic acid esters
New method for the steroid D ring closure

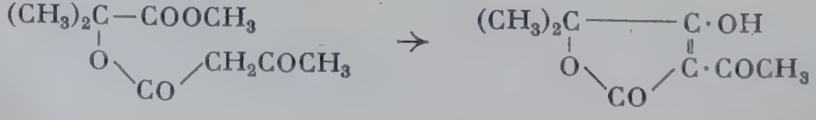
647.



2 *N* methanolic Na-methoxide added to a soln. of 150 mg. 2β,4b-dimethyl-1β-(2-tosyloxyethyl)-2-acetonyl-7-ethylenedioxy-1,2,3,4,4aα,4b,-5,6,7,8,10,10aβ-dodecahydrophenanthren-4α-ol in methanol, and stirred overnight at room temp. → 32 mg. 17-normal and 40 mg. 17-iso d,l-Δ^5-3-ethylenedioxypregnen-11α-ol-20-one. F. e. s. W. F. Johns, R. M. Lukes, and L. H. Sarett, Am. Soc. *76*, 5026 (1954).

α-Acetyltetronic acids

648.



$$\begin{array}{l}(CH_3)_2C-COOCH_3\\ \quad|\\ \quad O\diagdown\quad\diagup CH_2COCH_3\\ \qquad CO\end{array} \rightarrow \begin{array}{l}(CH_3)_2C\text{———}C\cdot OH\\ \quad|\qquad\qquad\ \ \|\\ \quad O\diagdown\quad\diagup C\cdot COCH_3\\ \qquad CO\end{array}$$

A soln. of methyl α-hydroxyisobutyrate acetoacetate in toluene added to a soln. of Na in ethanol, refluxed 4 hrs., and allowed to stand overnight→α-acetyl-γ,γ-dimethyltetronic acid. Y: 98%. F. e. s. R.N. Lacey, Soc. *1954*, 832.

Camps pyridone ring closure
s. *6*, 844; s. a. J. Org. Chem. *18*, 1516 (1953)

Sodium methoxide

4-Azafluoranthenes
s. *6*, 845

Potassium tert-butoxide *KOR*

Dieckmann cyclization
s. *9*, 934

Sodium/liq. ammonia *Na/NH₃*

Stereospecific acyloin condensation $\underline{|\text{—CH(OH)CO—}|}$
s. *9*, 935

Sodium carbonate Na_2CO_3

1,1-Nitroethylene derivatives from 1,2-nitroacetoxy compounds CHC(OAc) → C:C

$$ClCH_2CH(OAc)CH(NO_2)CH_3 \rightarrow ClCH_2CH{=}C(NO_2)CH_3$$

A stirred mixture of 1-chloro-3-nitro-2-butyl acetate, anhydrous Na-carbonate. and dry benzene refluxed 5-6 hrs. → 1-chloro-3-nitro-2-butene (startg. m. f. 614). Y: 72%. H. Shechter and F. Conrad, Am. Soc. *76*, 2716 (1954).

Azulenes – Dehydrogenation ○
s. *7*, 874

Potassium carbonate K_2CO_3

α,β-Ethyleneketones from β-hydroxyketones CHC(OH) → C:C
s. *9*, 936

Sodium acetate CH_3COONa

α,β-Ethylene-γ-diketones from α-hydroxy-γ-diketones
s. *6*, 826

1,1-Nitroethylene derivatives from 1,2-nitroacoxy compounds CHC(OAc) → C:C
s. *6*, 846

Potassium acetate CH_3COOK

1,2-Ionic elimination ←
Ethylene derivatives from sulfonic acid esters and halides
s. *10*, 654

Potassium cyanide *KCN*

Ring closure to isocyclics ○
with preceding replacement of bromine by cyano groups
s. *10*, 620

Sodium chloride s. under Zinc chloride, Aluminum chloride *NaCl*

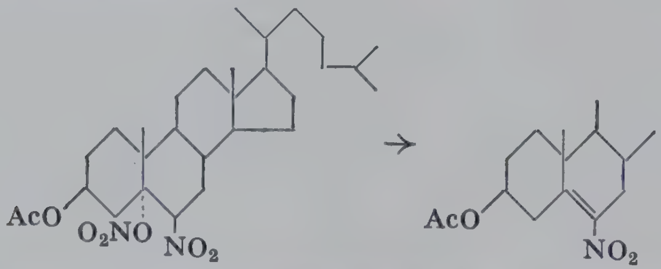
Sodium iodide *NaI*

Ethylenecarbohydrates C(OTs)C(OTs) → C:C
from di-p-toluenesulfonic acid esters
s. *6*, 847

Ammonia *NH_3*

1,1-Nitroethylene derivatives $CHC(ONO_2) \rightarrow C:C$
from 1,2-nitronitric acid esters

650.



NH_3-gas bubbled through an ice-salt cooled soln. of 6β-nitrocholestane-3β,5α-diol 3-acetate 5-nitrate in ether for ca. 1 hr. → 6-nitrocholesteryl acetate. Y: 95%. F. e. s. C. E. Anagnostopoulos and L. F. Fieser, Am. Soc. *76*, 532 (1954).

Pyridine s. a. under P_2O_5, PBr_3, $POCl_3$, $SOCl_2$, RSO_2Cl *C_5H_5N*

Ethylene derivatives from acoxy compounds with rearrangement ←
s. *6*, 864

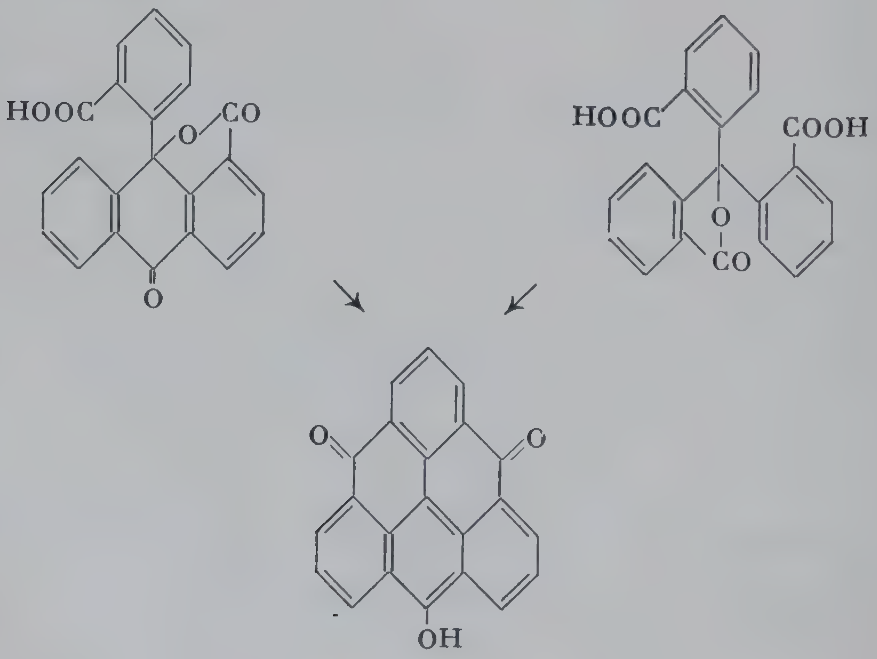
γ-Collidine ←

Dehydration of alcohols via methylsulfonic acid esters CHC(OH)→C:C
s. *8*, 887

Copper/sulfuric acid *Cu/H_2SO_4*

Extended quinones ←

651.



9-(o-Carboxyphenyl)oxanthranol-1-carboxylic acid lactone (prepn. s. 130) | Di-(o-carboxyphenyl)phthalide

and Cu-powder heated 1 hr. with concd. H_2SO_4 at 120° → 12-hydroxy-triangulene-4,8-quinone.

Y: almost 100%. | 3.8 g. from 5 g.

E. Clar and D. G. Stewart, Am. Soc. *75*, 2667 (1953).

Helinathrones via bianthraquinones
s. *8*, 888

Silver acetate CH_3COOAg

1,2-Ionic elimination ←
Ethylene derivatives from sulfonic acid esters and halides
s. *10*, 654

Cupric sulfate $CuSO_4$

Dehydration of alcohols CHC(OH) → C:C
s. *8*, 889

Cuprous chloride $CuCl$

Fumaric di-γ-enollactones ○
from α,β-ethylene-γ-ketocarboxylic acids
Dimerization
s. *8*, 890

Calcium oxide/sodium hydroxide $CaO/NaOH$

Ethylenecarbohydrates CHC(OTs) → C:C
from p-toluenesulfonic acid esters
s. *8*, 886

Zinc Zn

Isocyclics from ketones – Elbs pyrolysis ○
s. *9*, 937

Magnesium alkoxide $Mg(OR)_2$

Benzofurans
s. *7*, 875

Methylmagnesium bromide CH_3MgBr

Ethylene derivatives from sulfonic acid esters ←
Hydrolytic ring opening of isocyclics
s. *9*, 772

Zinc chloride $ZnCl_2$

Enediolethers from α-alkoxyacetals ←
s. *6*, 849

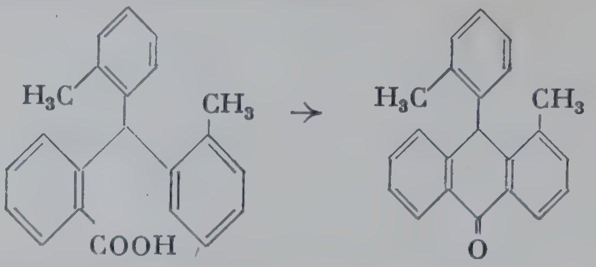
Anthracene ring ○
s. *6*, 848

N-Heterocyclics from hydroxycarboxylic acid amides
s. *9*, 956

Zinc chloride/sodium chloride *$ZnCl_2/NaCl$*

Cyclic ketones from carboxylic acids

652.



Anthrones. 2-(Di-o-tolylmethyl)benzoic acid, $ZnCl_2$, and NaCl heated with constant stirring to 220°, and maintained 15-20 min. at that temp. → 1-methyl-9-(o-tolyl)-10-anthrone (startg. m. f. 130). Y: 96%. E. Clar and D. G. Stewart, Am. Soc. *75*, 2667 (1953).

Lithium aluminum hydride *$LiAlH_4$*

Dienes from α,β-ethyleneketones COCH → CH:C

s. *7*, 874

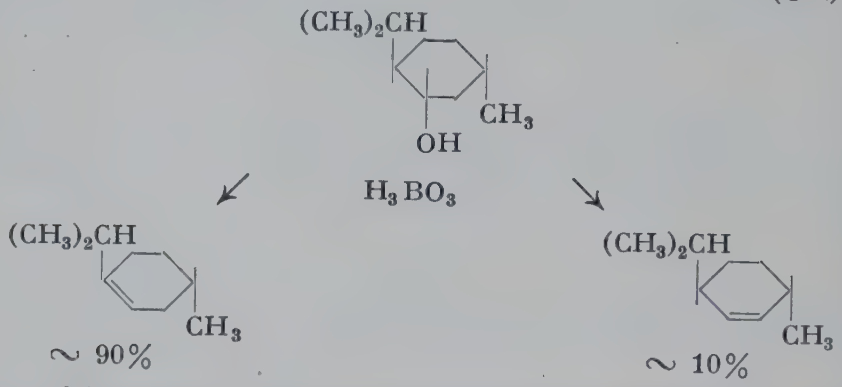
Indoles from oxindoles ←

s. *9*, 938

Boric acid *HBO_2*

Dehydration of alcohols CHC(OH) → C:C

653.



A mixture of l-menthol and boric acid slowly heated in an oil bath to 150-180° while water distils off, then the temp. slowly raised to 270° with distillation of the products → mixture of Δ^2- and Δ^3-menthenes (Y: 83-92%) consisting of 87-91% Δ^3-menthene, of which ca. 70% is racemized. F. e. s. G. L. O'Connor and H. R. Nace, Am. Soc. *77*, 1578 (1955); method s. W. Brandenberg and A. Galat, Am. Soc. *72*, 3275 (1950).

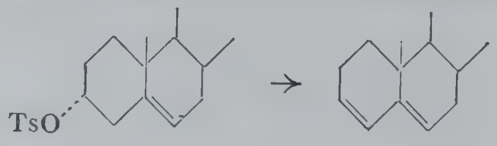
Alumina *Al_2O_3*

s. *9*, 981; s. a. D. S. Popplewell and R. G. Wilkins, Soc. *1955*, 2521

1,2-Ionic elimination ←

Ethylene derivatives from sulfonic acid esters and halides

654.

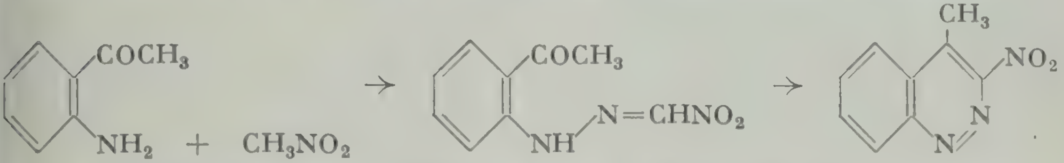


Dry cholest-5-en-3α-yl p-toluenesulfonate chromatographed on neutral Al_2O_3 (s. original) prepared in pentane, and eluted with the same solvent → cholesta-3.5-diene. Y: 94%.—Cholesta-3.5-diene is also obtained from the tosylate, mesylate, or chloride with K- or Ag-acetate in glacial acetic acid with 92-99% yield, since 1.2-ionic elimination proceeds with great ease. D. D. Evans and C. W. Shoppee, Soc. *1953*, 540.

Dienes from ketones with rearrangement ←
s. *8*, 891

3-Nitroquinolines ○
s. *6*, 850

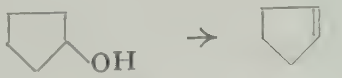
3-Nitrocinnolines from amines via nitroformaldehyde hydrazones
Diazotization by the Erban und Mebus "nitrite paste" procedure



A diazonium salt soln. prepared from o-aminoacetophenone hydrochloride and aq. Na-nitrite in aq. HCl below 5°, poured into a soln. of Na-isonitromethane, prepared by addition of alc. nitromethane to NaOH in ice-water, and stirred 1 hr. → crude nitroformaldehyde o-acetylphenylhydrazone (Y: 74-98%) dissolved in acetone, treated with activated alumina, and allowed to stand 60 hrs. at room temp. → 4-methyl-3-nitrocinnoline (Y: 59%).—The diazotization of o-aminobenzaldehyde by the usual procedures was unsuccessful. The "nitrite paste" procedure (F. Erban and A. Mebus, Chem. Z. *31*, 1101 (1907)) was therefore used whereby a slurry of o-aminobenzaldehyde and Na-nitrite made with a small amount of water is added at 0° to a mixture of concd. HCl and ice. Nitroformaldehyde o-formylphenylhydrazone was obtained in yields of 53-63%. F. e. s. H. E. Baumgarten and M. R. DeBrunner, Am. Soc. *76*, 3489 (1954).

Alumina-silica-carbon Al_2O_3-SiO_2-C

Dehydration of alcohols CHC(OH) → C:C



The vapor from boiling cyclopentanol carried by a slow N_2-stream at 380-400° through a tube charged with a catalyst prepared from Al_2O_3, kieselguhr and cork powder (s. original) → cyclopentene. Y: 81%. A. Stoll, A. Lindenmann, and E. Jucker, Helv. *36*, 268 (1953).

Aluminum alkoxide $Al(OR)_3$

Keteneacetals from orthocarboxylic acid esters $CHC(OR)_3 \rightarrow C{:}C(OR)_2$
s. *7*, 876

Aluminum phosphate/water glass

Alkoxydienes from alkoxyacetals $CHC(OR)_2 \rightarrow C{:}C(O$
s. *6*, 851

Boron flüoride *B*

Dehydration of alcohols $CHC(OH) \rightarrow C$
s. *8*, 892

Aluminum chloride *Al*

Cyclodehydration – Isocyclics from ketones
s. *9*, 939

Aluminum chloride/sodium chloride $AlCl_3/Na$

Reactions with fused aluminum chloride/sodium chloride
Cyclic ketones from carboxylic acids
Ring closure by isomerization
s. *8*, 893

Anthraquinones – Alkyl migration
s. *9*, 940

Carbon

Ketenes from carboxylic acid anhydrides $(RCH_2CO)_2O \rightarrow 2RCH{:}C{:}$
s. *9*, 941

Glycerol $CH_2(OH)CH(OH)CH_2(O$

Chromone ring from o-acoxyketones
s. *7*, 877

Piperidinium acetate

Cyclic *α*,*β*-ethylenealdehydes from dialdehydes
s. *9*, 942

Ring closure with
Acetic anhydride $(CH_3CO)_2$
s. *9*, 943

Acetic anhydride/sulfuric acid $(CH_3CO)_2O/H_2S$
s. Sulfuric acid/acetic anhydride

Phthalic anhydride/sulfonic acids

Dehydration of alcohols $CHC(OH) \rightarrow C{:}$
s. *7*, 878

Acetic acid CH_3COO

Dehydration $CHC(OH) \rightarrow C{:}$
s. *6*, 628; partial dehydration s. *9*, 944

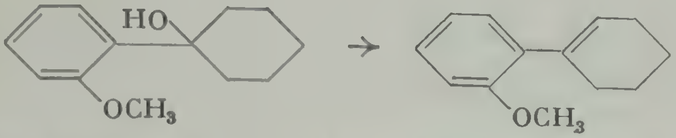
Phenols by dehydration with rearrangement
s. *9*, 945

Dienes from alkoxyethylene derivatives
s. *9*, 950

Oxalic acid *$(COOH)_2$*

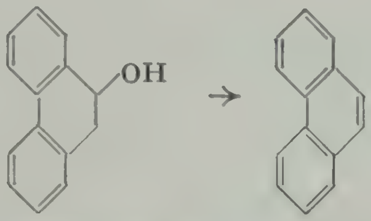
Dehydration CHC(OH) → C:C

s. *6*, 852



Azeotropic water separation. 1-o-Methoxyphenylcyclohexanol distilled with anhydrous oxalic acid and toluene until no more water is collected in the azeotropic separator → 1-o-methoxyphenylcyclohexene. Y: ca. 100%. D. Ginsburg et al., Soc. *1951*, 516; Am. Soc. *76*, 3625 (1954).

Acetyl chloride *CH_3COCl*



Crude 9,10-dihydro-9-phenanthrol refluxed 1 hr. in acetyl chloride → phenanthrene. Y: 85%. A. J. Weinheimer, S. W. Kantor, and C. R. Hauser, J. Org. Chem. *18*, 801 (1953).

Acoxy-2-ethylenes from glycols ←

s. *8*, 894

Quaternary cyclic enammonium salts from ethanolbetainecarbeniates ←

s. *8*, 711

Stearoyl and lauroyl chloride *RCOCl*

Dehydration CHC(OH) → C:C

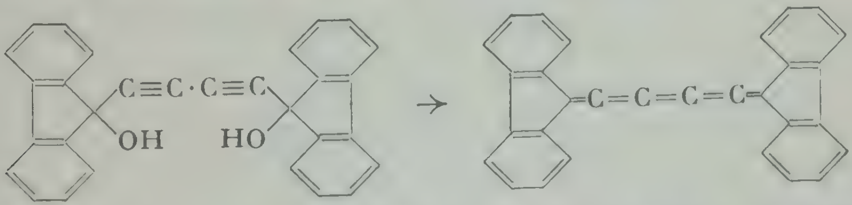
s. *7*, 879

Benzoyl chloride *C_6H_5COCl*

s. *6*, 853

Stannous chloride *$SnCl_2$*

Cumulenes from mono-, di-, and tri-acetylenediols ←



$SnCl_2 \cdot 2H_2O$ and concd. HCl added to a mixture of bis(diphenylene)-hexadiynediol and chloroform, shaken 5 hrs. → bis(diphenylene)hexapentaene. Y: 94.5%.—The use of $SnCl_2$ obviates exclusion of air as is necessary with $CrCl_2$ or VCl_2. F. e. and procedures s. R. Kuhn and H. Krauch, B. *88*, 309 (1955).

Stannic chloride s. under $POCl_3$, PCl_5 *SnC*

Phosphorus pentoxide *P_2O*

Dehydration CHC(OH) → C:(

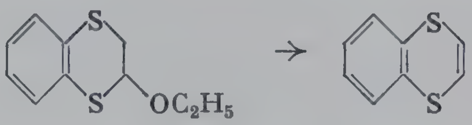
s. *10*, 667; s. a. H. M. Walborsky, M. Baum, and D. F. Loncrini, Am Soc. *77*, 3637 (1955)

Wagner rearrangement – Dehydration-rearrangement ←
s. *8*, 895

1,4-Oxathienes from 2-alkoxy-1,4-oxathianes and reverse reaction ←
s. *7*, 880

Benzo-1,4-dithiins from 2-alkoxybenzo-1,4-dithianes

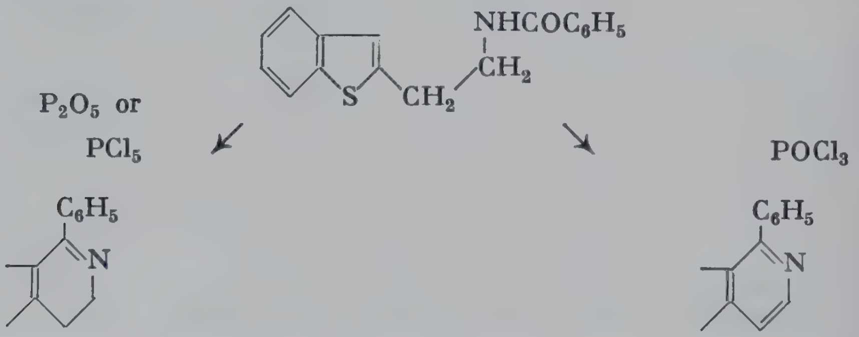
660.



2-Ethoxybenzo-1,4-dithiane and a little P_2O_5 heated at 170-175° for ca 2 hrs. with distillation of the ethanol formed → benzo-1,4-dithiin. Y: 72%. W. E. Parham, T. M. Roder, and W. R. Hasek, Am. Soc. *75*, 164 (1953).

Bischler-Napieralski ring closure

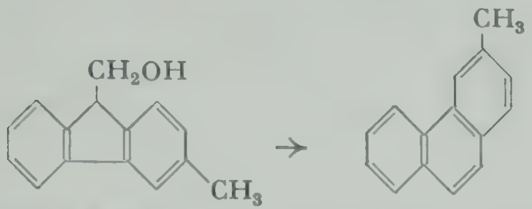
661.



A mixture of N-benzoyl-2-thianaphthenethylamine, P_2O_5, xylene, and *glass balls* stirred 7 hrs. on a steam bath under anhydrous conditions, and the product isolated as the hydrochloride → 1-phenyl-3,4-dihydrothianaphtheno[3,2-c]pyridine hydrochloride. Y: 87%.—The glass balls prevent the deposit of the phosphate salt of the basic product, insoluble in xylene, on the suspended particles of P_2O_5. PCl_5 at room temp. gives 78% yield. With $POCl_3$, 71% yield of fully aromatized product is obtained. D. B. Capps and C. S. Hamilton, Am. Soc. *75*, 697 (1953).

Isoquinolines s. *5*, 621; 9H-pyrid[3,4-b]indoles s. C. F. Huebner, H. A. Troxell, and D. C. Schroeder, Am. Soc. *75*, 5887 (1953)

Wagner rearrangement – Phenanthrenes from fluorenes ←



A mixture of 3-methyl-9-fluorenylcarbinol, xylene, and P_2O_5 refluxed 30 min. → 3-methylphenanthrene. Y: 88%. Also labeled compounds s. C. J. Collins and B. M. Benjamin, Am. Soc. *75*, 1644 (1953).

Isocyclics from lactones ←
s. *8*, 896

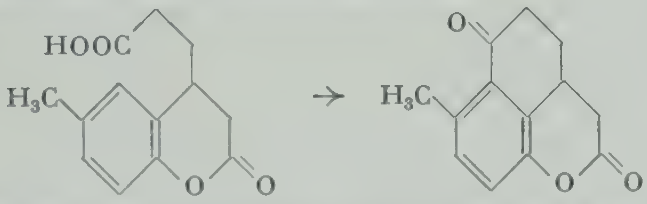
Phosphorus pentoxide/pyridine P_2O_5/C_5H_5N

Enolethers from acetals $CHC(OR)_2 \rightarrow C{:}C(OR)$
s. *9*, 946

Phosphorus pentoxide/phosphoric acid P_2O_5/H_3PO_4

Isocyclics from ketones ○
s. *8*, 897

Cyclic ketolactones from carboxylactones



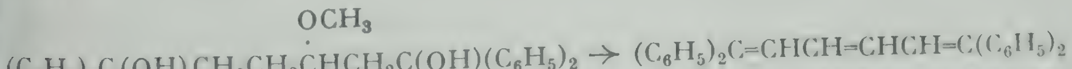
β-(6-Methyl-3,4-dihydro-4-coumarin)propionic acid added to a mixture of P_2O_5 and 85%-H_3PO_4 (homogenized by heating 2 hrs. at 100°), and heated 3 hrs. at 100° with occasional swirling → 4-keto-5-methyl-8-hydroxy-1,2,3,4-tetrahydro-1-naphthylacetic acid lactone. Y: 80%. A. S. Dreiding and A. J. Tomasewski, Am. Soc. *76*, 540 (1954).

Cyclic ketones from carboxylic acid esters
s. *8*, 898

3,4-Dihydrophenanthridones
Dicarboxylic acid imides from dicarboxylic acids
s. *7*, 881

Metaphosphoric acid $(HPO_3)_3$

Dehydration with simultaneous formation of ethylene derivatives from ethers ←



$$(C_6H_5)_2C(OH)CH_2CH_2\overset{OCH_3}{\dot{C}H}CH_2C(OH)(C_6H_5)_2 \rightarrow (C_6H_5)_2C{=}CHCH{=}CHCH{=}C(C_6H_5)_2$$

A soln. of d,l-1,1,6,6-tetraphenyl-3-methoxy-1,6-hexanediol in metaphosphoric acid heated slowly to 70° → 1,1,6,6-tetraphenyl-1,3,5-hexatriene. Y: almost 100%. M. Viscontini and H. Köhler, Helv. *37*, 41 (1954).

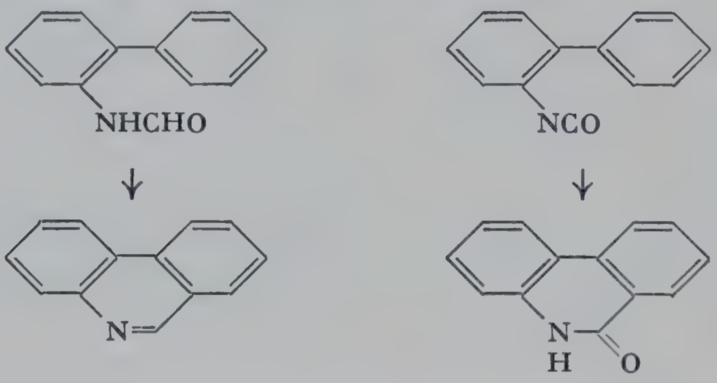
Ring closures with
Polyphosphoric acid $H(PO_3H)_xOH$
s. *8*, 899

Isocyclics from oxo compounds ○
s. *8*, 899; s. a. C. R. Hauser and J. G. Murray, Am. Soc. *77*, 3858 (1955)

Cyclic ketones from carboxylic acids
s. *6*, 854; *8*, 899; *9*, 947; s. a. Org. Synth., Coll. Vol. III, 798 (1955); D. A. Shirley and W. L. Dean, Am. Soc. *77*, 6077 (1955); 8-membered ring s. A. C. Cope and R. D. Smith, Am. Soc. *77*, 4596 (1955)

Phenanthridines – Lactams from isocyanates

665.



A mixture of polyphosphoric acid and

2-formamidobiphenyl heated 1 hr.	o-biphenyl isocyanate heated 2 hrs.

↙ at 140-160° with stirring ↘

phenanthridine. Y: 93.4%.	phenanthridone. Y: 87.3%.

E. C. Taylor, Jr., and N. W. Kalenda, Am. Soc. *76*, 1699 (1954).

Polyphosphoric acid/phosphorus oxychloride $H(PO_3H)_xOH/POCl_3$
s. Phosphorus oxychloride/polyphosphoric acid

Phosphoric acid H_3PO_4

Dehydration of stereoisomeric cyclic alcohols CHC(OH) → C:C
s. *6*, 867

Phosphorus diiodide P_2I_4

Ethylene derivatives from diols – Polyenes ←
s. *8*, 902

Phosphorus tribromide PBr_3

Phenanthrenes from fluorenes ←
Intracationic isomerization – Retropinacol type rearrangement
s. *8*, 900

Phosphorus tribromide/pyridine PBr_3/C_5H_5N

1,2,3-Trienes from 2-acetylene-1,4-diols C(OH)·C⋮C·C(OH) → C:C:C:C
s. *9*, 948

Phosphorus oxychloride $POCl_3$

Oxazoles from oxazolidones ←
s. *6*, 856

Bischler-Napieralski ring closure ○
Isoquinolines s. *7*, 882

Acridones
s. *1*, 749; s. a. G. Stapleton and A. J. White, J. Am. Pharm. Assoc. *43*, 193 (1954)

Benzo[a]quinolizine ring
s. *9*, 949

Phosphorus oxychloride/pyridine $POCl_3/C_5H_5N$

Dehydration of alcohols CHC(OH) → C:C
s. *7*, 883; s. a. I. A. Favorskaya and L. V. Fedorova, ЖК. *24*, 242 (1954); C. A. *49*, 4538i; A. Mondon, B. *88*, 724 (1955)

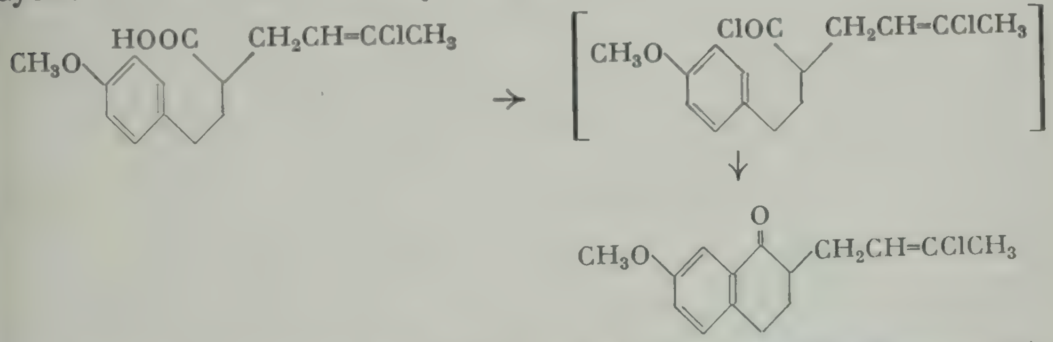
Dienes from 3-alkoxyethylene derivatives ←
s. *9*, 950

Phosphorus oxychloride/stannic chloride $POCl_3/SnCl_4$

Phenanthridines ○
s. *7*, 884

Phosphorus pentachloride PCl_5

Cyclic ketones from carboxylic acids



PCl_5 added portionwise with stirring to a soln. of α-(3-chlorocrotyl)-γ-(p-anisyl)butyric acid in dry benzene, then distilled, at first under atmospheric pressure finally in vacuo → 2-(3-chlorocrotyl)-7-methoxy-3,4-dihydro-1(2H)-naphthalenone. Y: 80.5%. G. T. Tatevosyan, P. A. Zagorets, and A. G. Vardanyan, ЖК. *23*, 941 (1953); C. A. *48*, 7593b.

Dehydration with ring contraction ←
s. 8, 901

Phosphorus pentachloride/stannic chloride $PCl_5/SnCl_4$

Cyclic ketones from carboxylic acids ○
s. *7*, 325

Vanadium dichloride

Ethylene derivatives from diols – Polyenes
s. *8*, 902

Sulfur

Aromatization of cyclic alcohols
s. *7*, 885; s. a. M. C. Kloetzel, J. E. Little, Jr., and D. M. Fisch, J. Chem. *18*, 1511 (1953)

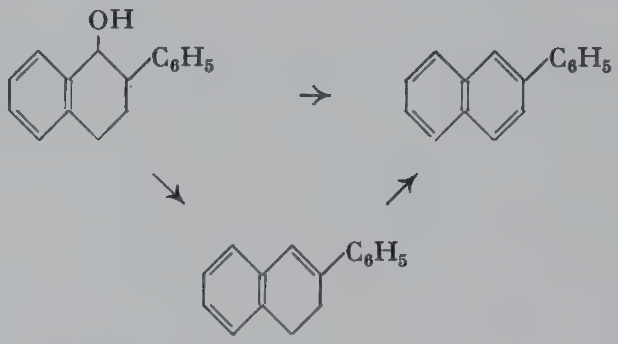
Hydrosulfite *S_2*

New indigo synthesis
Reductive ring closure to N-heterocyclics
s. *7*, 886

Thionyl chloride *S*

Aromatization, dehydration of alcohols, and dehydrogenation

667.



2-Phenyl-1-tetralol

allowed to react with $SOCl_2$ for 1 hr., then refluxed for the same period

shaken 5 hrs. with P_2O_5 in benzene → dihydro-2-phenylnaphthalene (1.84 2.00 g.) refluxed 15 hrs. with chloranil sulfur-free xylene

↘ ↙

Y: 90% 2-phenylnaphthalene. Y: 9

N. Campbell and D. Kidd, Soc. *1954*, 2154.

Thionyl chloride/pyridine *$SOCl_2/C_5$*

Dehydration of alcohols CHC(OH) →
Acoxy-2-ethylenes from glycol monoesters
s. *7*, 239

Thionyl chloride/sulfuric acid *$SOCl_2/H_2$*

Cyclic diketones from carboxylic acid anhydrides via cyclic ketocarboxylic acids
s. *8*, 903

p-Toluenesulfonyl chloride/pyridine *RSO_2Cl/C_5*

Dehydration of alcohols CHC(OH) →
s. *8*, 904

Sodium hydrogen sulfate $NaHSO_4$

Enolethers from acetals $\mathrm{CHC(OR)_2 \rightarrow C{:}C(OR)}$

s. *6*, 182; s. a R. A. Raphael and C. M. Roxburgh, Soc. *1955*, 3405

Potassium hydrogen sulfate $KHSO_4$

Ethylene derivatives $\mathrm{CHC(OH) \rightarrow C{:}C}$
from ketones via sec. alcohols
s. *9*, 951

Selective dehydration
Branched carbon chains s. *7*, 887

Potassium hydrogen sulfate/acetic anhydride $KHSO_4/(CH_3CO)_2O$

Dehydration of alcohols
s. *9*, 952

Sulfonic acids/phthalic anhydride ←
s. Phthalic anhydride/sulfonic acids

p-Toluenesulfonic acid *TsOH*
s. *7*, 891

Dehydration-rearrangement ←
s. *9*, 958

Sulfuric acid H_2SO_4

Dehydration of alcohols $\mathrm{CHC(OH) \rightarrow C{:}C}$

s. *5*, 627; s. a. J. D. Edwards and J. L. Cashaw, J. Org. Chem. *20*, 847 (1955)

Isocarbostyrils from 4-hydroxy-1,2,3,4-tetrahydroisoquinolones
s. *8*, 407

Dehydration-rearrangement ←
s. *8*, 906

Ethyleneketones from hydroxyenolethers ←
s. *10*, 516

Dienes from oxido compounds ←
s. *8*, 907

Cyclic ketones from carboxylic acids ○
s. *2*, 796/7; s. a. A. L. Green and D. H. Hey, Soc. *1954*, 4306

Anthraquinone ring closure
s. *2*, 797; imidazo[4,5-b]anthraquinones s. L. S. Efros, B. A. Porai-Koshits, and S. G. Farbenshtein, Ж. *23*, 1691 (1953); C. A. *48*, 13686e.

Cyclic ketones from carboxylic acid esters
s. *7*, 785

Hydroxyquinones from dicarboxylic acids
s. *8*, 908

Dicarboxylic acid anhydrides from
carboxylic acid esters via α-keto-β-dicarboxylic acid esters
Bougault ring closure
s. *6*, 858

Benzofurans
s. *9*, 953

Synthesis of O-heterocyclics with diketene
4-Methylcoumarins from phenols and diketene via arylacetoacetic acid esters
s. *9*, 954

Xanthylium salts
s. *6*, 162

Pyridine ring from enamines
s. *9*, 955

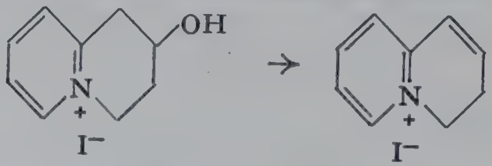
N-Heterocyclics from hydroxycarboxylic acid amides
s. *9*, 956

Thiaxanthones
s. *8*, 909

Sulfuric acid/acetic anhydride — $H_2SO_4/(CH_3CO)_2O$

Dehydration — CHC(OH) → C:C
Quaternary cyclic N-condensed ammonium salts

668.



A mixture of 2-hydroxy-1,2-dihydro-3H,4H-quinolizinium iodide and acetic anhydride containing one drop of concd. H_2SO_4 refluxed 5 min. → 3H,4H-quinolizinium iodide. Y: 98%. V. Boekelheide and W. G. Gall, Am. Soc. *76*, 1832 (1954).

Sulfuric acid/acetic acid — H_2SO_4/CH_3COOH

Dehydration-rearrangement ←
s. *7*, 888

Fluorosulfonic acid — FSO_3H

Cyclic ketones from carboxylic acids ○
s. *8*, 910

Chlorosulfonic acid — $ClSO_3H$

Anthrapyridonacridones via anthrapyridones
s. *6*, 859

Selenium dioxide — SeO_2

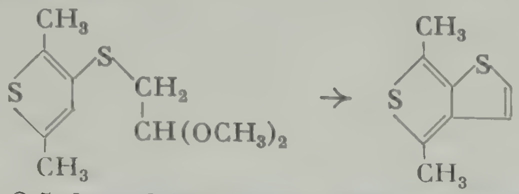
Dehydration of alcohols — CHC(OH) → C:C
s. *9*, 957

Iodine — *I*
s. *6*, 860

Hydrofluoric acid — *HF*

Isocyclics from alcohols ○
with preceding synthesis of tert. alcohols from ketones
s. *8*, 911

Ring closure with acetals



β-Dimethoxyethyl 2,5-dimethylthienyl sulfide in anhydrous HF kept 5 hrs. at 70-80°, and the product isolated as the picrate → 2,5-dimethylthiopheno-2′,3′:3,4-thiophene picrate. Y: 48%. O. Dann and W. Dimmling, B. *87*, 373 (1954).

Cyclic ketones from carboxylic acids and carboxylic acid chlorides
s. *6*, 861

Hydrochloric acid *HCl*

Dehydration of alcohols CHC(OH) → C:C
s. *6*, 862; *8*, 912 s. a. B. D. Astill and V. Boekelheide, Am. Soc. *77*, 4079 (1955)

Phenols by dehydration
s. *8*, 913

Ethylenecarboxylic acids from hydroxycarboxylic acid esters
s. *9*, 25

Dehydration with simultaneous esterification
s. *6*, 689

Dehydration-rearrangement ←
s. *9*, 958

Ethylene derivatives from ethers CHC(OR) → C:C
s. *6*, 863

Ethylene derivatives from acoxy compounds CHC(OAc) → C:C
s. *6*, 864; s. a. Q. R. Pedersen and C. T. Chen, Am. Soc. *77*, 2557 (1955)

***α,β*-Ethylenealdehydes from alkoxyacetals** CH:CHCHO
s. *7*, 889

Indenes from pinacols – Pinacol rearrangement ○
s. *8*, 914

Aromatization by elimination of an oxygen bridge ←
s. *9*, 959

Isocyclics from O-heterocyclics ←
s. *6*, 865

Hydrobromic acid *HBr*

1H-Indeno[2,1-c]pyridines ○
s. *6*, 866

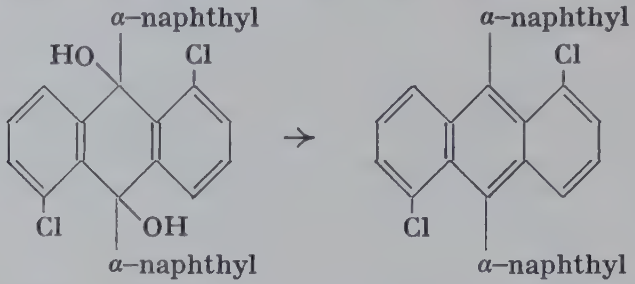
Hydrobromic acid/acetic acid HBr/CH_3COOH

Isocyclics from ketones
Anthracene ring s. *5*, 642; s. a. F. A. Vingiello, A. Bořkovec, and J. Schulman, Am. Soc. *77*, 2320, 4823 (1955); phenanthrene ring s. J. Colonge and A. Arsac, Bl. *1954*, 445

Hydriodic acid *HI*

Anthracenes from 9,10-dihydro-9,10-dihydroxyanthracenes ←

670.



A suspension of 25 g. 1,5-dichloro-9,10-dihydro-9,10-di-(1′-naphthyl)-anthracene-9,10-diol in acetic acid and 55%-HI refluxed 15 min. → 21 g. 1,5-dichloro-9,10-di-(1′-naphthyl)anthracene. E. Clar, W. Kelly, and J. W. Wright, Soc. *1954*, 1108.

Via intermediates *v.i.*

Dehydration of alcohols CHC(OH) → C:C
s. *8*, 887; of stereoisomeric cyclic alcohols s. *6*, 867

Dehydration of alcohols via ethyl carbonates
s. *8*, 915

Ethyleneamines from aminoalcohols
s. *7*, 890

Dibenz[b,f]oxepins ←
Sec. alcohols from ketones – Dehydration
s. *7*, 891

Ethylene derivatives from glycols ←
or glycol monoethers via 1,2-dibromides
Synthesis of olefinic acids
s. *8*, 916

Ketenes from carboxylic acids CHCOOH → C:C:O
via α-bromocarboxylic acid bromides
s. *9*, 960

Cyclic ketones from carboxylic acids ○
Naphtho[1,8-bc]thiapyrans s. *6*, 889

o-Hydroxy-β-diketones from o-acoxyketones
Baker-Venkataraman transformation – Chromone ring
s. *6*, 868

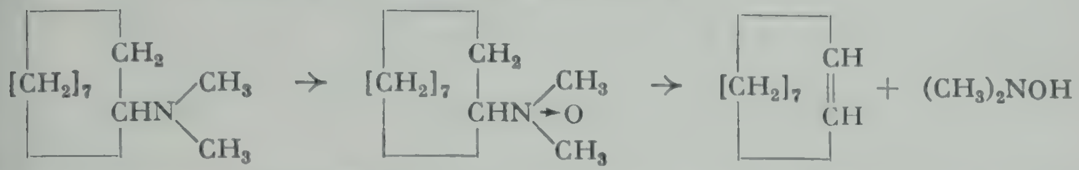
Nitrogen ↑ CC ⇑ N

Without additional reagents *w.a.r.*

(Sym.) α-dinitriles from ketones ←
via sym. hydrazodinitriles and sym. azodinitriles
Dimerization
s. *6*, 869

Hydrocarbons from aliphatic azo compounds ←
s. *8*, 621

Ethylene derivatives from tert. amines via N-oxides and by Hofmann degradation $CHC(NR_2) \rightarrow C{:}C$



cis-trans-Isomers. 30%-H_2O_2 added in small portions at 0° with swirling during 10 min. to a soln. of cyclononyldimethylamine in methanol, allowed to come to room temp. and to stand 25 hrs., at which time the test for the amine with phenolphthalein is negative, stirred overnight with a little Pd-black (prepn. s. R. Feulgen, B. *54*, 360 (1921)) added as an aq. suspension, to decompose excess H_2O_2, the soln. of the resulting amine oxide (Y: 96% when isolated as the picrate) concentrated under reduced pressure, and the residue heated at 12 mm., whereby decomposition occurs during 30 min. at a bath temp. of 80-95° → *trans*-cyclononene (Y: 80-90%) and N,N-dimethylhydroxylamine (Y: 96% as the hydrochloride. F. e. and comparison with the Hofmann degradation regarding the formation of *cis-trans*-isomers s. A. C. Cope, D. C. McLean, and N. A. Nelson, Am. Soc. *77*, 1628 (1955).

Hofmann degradation of quaternary ammonium salts via quaternary ammonium hydroxides $CHC(\overset{+}{N}\langle) \rightarrow C{:}C$
s. *8*, 917

Acetylene derivatives from quaternary cyclic enammonium salts $CH{:}C(\overset{+}{N}\langle) \rightarrow C{\vdots}C$
s. *8*, 918

Irradiation ←

Ketenes and carboxylic acids from α-diazoketones ←
s. 8, 919

Carboxylic acid esters and amides from α-diazoketones via ketenes ←
s. *8*, 920

Sodium hydroxide *NaOH*

Hofmann degradation of quaternary ammonium salts $CHC(\overset{+}{N}\langle) \rightarrow C{:}C$
s. *10*, 187

α,β-Ethyleneoximes from quaternary β-oximinoammonium salts
s. *10*, 239

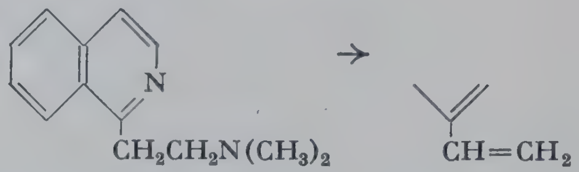
α,β-Ethylenecarboxylic acids from betaines $CH{:}CHCOOH$
s. *8*, 921

Potassium hydroxide *K*

Hofmann degradation
Ethylene derivatives from amines $CHC(N\langle) \rightarrow C$
s. *6*, 722

Ethylene derivatives from tert. amines $CHC(NR_2) \rightarrow C$

672.



1-(β-Dimethylaminoethyl)isoquinoline distilled from powdered KO and a trace of N-phenyl-β-naphthylamine as polymerization inhibit → 1-vinylisoquinoline. Y: 70%. V. Boekelheide and A. L. Sieg, J. Or Chem. *19*, 587 (1954).

Aldehydes, acetylene derivatives, and vinyl ethers from 3-nitroso-2-oxazolidones – Rearrangement
s. *8*, 922

Potassium hydroxide/platinized asbestos
s. Platinized asbestos/potassium hydroxide

Sodium/ethylene glycol *Na/HOCH₂CH₂O*

Alkaline decomposition of p-toluenesulfonylhydrazones
s. *9*, 961

Sodium nitrite *NaN*

Ring closure by diazo coupling

Fluorenone ring closure
s. *2*, 810; s. a. Helv. *38*, 393 (1955)

Sodium chloride/aluminum chloride *NaCl/AlC*
s. Aluminum chloride/sodium chloride

Copper *C*

Pschorr ring closure
s. *6*, 870; in dimethylformamide s. H. Rapoport, R. H. Allen, an M. E. Cisney, Am. Soc. *77*, 670 (1955)

Silver oxide *Ag₂*

Hofmann degradation of quaternary ammonium salts $CHC(\overset{+}{N}\langle) \rightarrow C$:
s. *7*, 811; *10*, 671; s. a. R. T. Arnold and P. N. Richardson, Am. So *76*, 3649 (1954); A. R. Battersby and R. Binks, Soc. *1955*, 2896

Calcium oxide *Ca*

Oxindoles from carboxylic acid hydrazides
s. *8*, 923

Mercuric oxide *HgO*

Acetylene derivatives from dihydrazones $C(:N\cdot NH_2)C(:N\cdot NH_2) \rightarrow C\vdots C$
s. *8*, 924

Boron fluoride *BF_3*

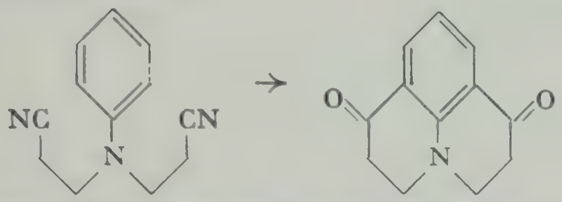
α,β-Nitroethylene derivatives from 1,2-nitramines $CHC(NR_2) \rightarrow C:C$
s. *8*, 925

Aluminum chloride/sodium chloride *$AlCl_3/NaCl$*

Isatins from amidines via 2-iminoisatins ○
s. *6*, 871

Aluminum chloride/hydrochloric acid *$AlCl_3/HCl$*

Cyclic ketones from nitriles



1,6-Diketojulolidines. Bis-2-cyanoethylaniline added to a mixture of $AlCl_3$, Chlorobenzene, and some concd. HCl, then heated 8.5 hrs. at 170° with stirring → 1,6-diketojulolidine. Y: 75%. F. e. s. J. T. Braunholtz and F. G. Mann, Soc. *1953*, 1817; *1952*, 3046.

Acetic acid *CH_3COOH*

Acylated enamines from 1,1-di(acylamino) compounds $CHC(NHAc)_2 \rightarrow C:C(NHAc)$
s. *7*, 892

Fischer indole ring synthesis ○
s. *6*, 872

Oxalic acid *$(COOH)_2$*

Ethylene derivatives from amines $CHC(NR_2) \rightarrow C:C$
s. *7*, 893

Phosphorus pentoxide *P_2O_5*

Ethylene derivatives from acylamines $CHC(NHAc) \rightarrow C:C$
s. *6*, 873

Phosphoric acid *H_3PO_4*

Carbazoles from 1,2,3-triazoles according to Graebe-Ullmann ←
s. *6*, 874

Phosphorus oxychloride *$POCl_3$*

3,4-Dihydroisoquinolines from amidines ○
s. *7*, 894

Sulfuric acid *H_2SO_4*

Fischer indole ring synthesis
s. *8*, 740, 926; also indoles from pyridazinones s. *10*, 674

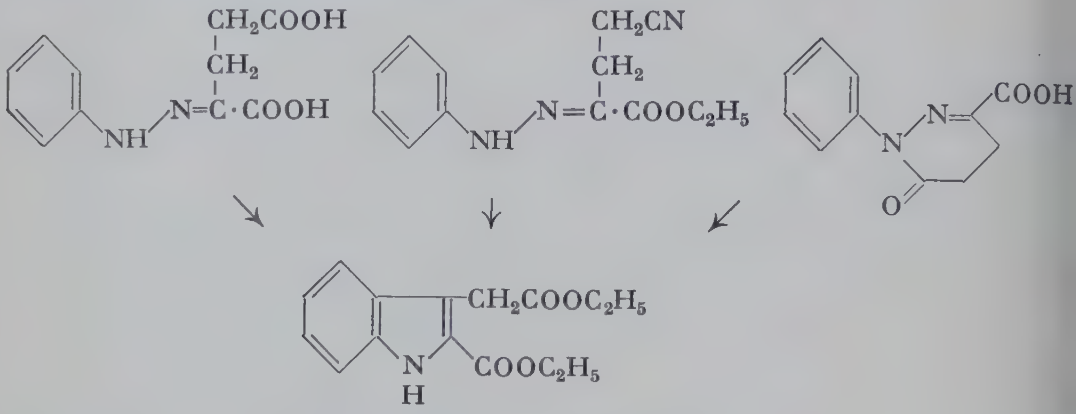
Octahydroquinolines
s. *7*, 895

Hydrochloric acid *HC*

Fischer indole ring synthesis with aldehyde hydrazones
s. *9*, 962; s. a. Am. Soc. *77*, 4319 (1955)

Fischer indole ring synthesis – Indoles from pyridazinones
2-Carbalkoxyindole-2-acetic acid esters

674.



HCl-gas introduced into a sol. of

α-ketoglutaric acid phenylhydrazone in abs. alcohol for 5 min. with heating on a water bath, heating continued for 30 min. →	ethyl β-cyanomethylpyruvate phenylhydrazone in aq. alcohol at first in the cold, then heated 50 min. on a water bath ↓	1-phenylpyridazinone-3-carboxylic acid in abs. alcohol at first in the cold, then heated 30 min. on a water bath →

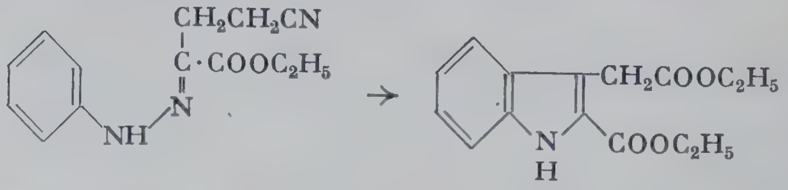
ethyl 2-carbethoxyindolyl-3-acetate.

Y: 94.3% 95.8% 99.7%.

In the closure of an indole ring from arylhydrazones of 2-oxoglutaric acid, electrophilic groups in the benzene ring hinder the reaction, while nucleophilic groups aid it. F. e. from carboxylic acids and pyridazinones with H_2SO_4 s. V. V. Feofilaktov and N. K. Semenova, Ж. *23*, 644 (1953); C. A. *48*, 7600a; Fischer indole ring synthesis s. a. E. Shaw, Am. Soc. *77*, 4319 (1955).

Fischer indole ring synthesis
with simultaneous formation of carboxylic acid esters from nitriles

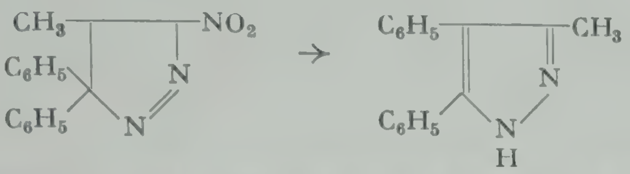
675.



Crude ethyl γ-cyano-α-ketopropionate phenylhydrazone in ethanol treated with dry HCl for 20 min. in the cold, then with heating on a water bath for ca. 1 hr. → crude ethyl 2-carbethoxy-3-indolylacetate.

Y: 90-95%. V. V. Feofilaktov and N. K. Semenova, Sint. Org. 2, 63 (1952); C. A. 48, 666c.

Pyrazoles from nitropyrazolines ←
s. 7, 713



with rearrangement. Concd. HCl added to a soln. of 3-nitro-4-methyl-5,5-diphenylpyrazoline in warm ethanol, and heated 2 hrs. on a steam bath until a negative starch-iodide test is obtained → 3-methyl-4,5-diphenylpyrazole. Y: 90%. F. e. s. W. E. Parham and W. R. Hasek, Am. Soc. 76, 799 (1954).

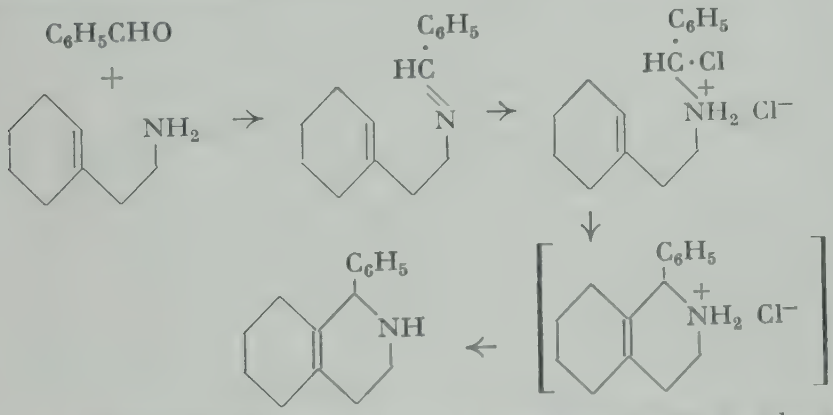
3-Halogenopyrazoles ○
from 1-halogeno-1-nitro-1,2-ethylene derivatives
s. 8, 737

Platinized asbestos/potassium hydroxide ←
Cyclopropanes from
α,β-ethyleneoxo compounds via 2-pyrazolines
s. 8, 927; cf. G. Laber, A. 588, 79 (1954)

Halogen ↑ CC ⇑ Hal

Without additional reagents *w.a.r.*
Thermal dehydrohalogenation of polyhalides CHCHal → C:C
s. 7, 896; partial dehydrohalogenation s. 8, 928

Octahydroisoquinolines via azomethines and α-chloramines ○



An alc. soln. of cyclohexenylethylamine combined with an alc. soln. of benzaldehyde, and allowed to stand 12 hrs. → N-benzylidenecyclohexenylethylamine (Y: 97%) dissolved in benzene, and a moderate stream of dry HCl passed into the boiling soln. with stirring for ca. 45 min. → N-(α-chlorobenzyl)cyclohexenylethylamine hydrochloride

(Y: 88%) heated slowly in an oil bath to 200°, allowed to cool af
ca. 45 min., dissolved in methanol with warming, treated with meth
nolic KOH, and refluxed 1 hr. → 1-phenyl-1,2,3,4,5,6,7,8-octahydrois
quinoline (Y: 93%). Overall Y: 80%. F. e. and methods s. R. Gre
et al., A. *581*, 85 (1953).

Lithium

Dihydrophenanthrene ring
s. *6*, 875

Sodium hydroxide *NaC*

9-Nitroanthracenes from 9-nitro-10-chloro-9,10-dihydroanthracenes
s. *7*, 414

Potassium hydroxide *KO*

Dienes from β,γ-ethylenehalides CHCHal → C
s. *7*, 897

1,2-Ethylene-1,1-dihalides from 1,1,1-trihalides
s. *4*, 232

Acetylene derivatives from α,β-ethylenehalides CH:CHal → C
Selective dehydrohalogenation
s. *6*, 876

α,β-Ethyleneoximes from α-nitrosohalides
s. *8*, 929

Acetylene derivatives from 1,2-dichlorides CHClCHCl → C
s. *6*, 877

Ethylene derivatives from polyhalides CHalCHal → C:

678. $CCl_2{=}CCl{\cdot}CCl_2{-}CCl_2{-}CCl{=}CCl_2 \rightarrow CCl_2{=}CCl{-}CCl{=}CCl{-}CCl{=}CCl_2$

Alc. 2 *N* KOH added dropwise below 40° to a soln. of perchlorohex
diene in acetone → α-perchlorohexatriene. Y: 90%. A. Roedig, G. Vos
and E. Kuchinke, A. *580*, 24 (1953).

Chalcones from α,β-dibromoketones CHBrCHBrCO → CH:CHC
s. *7*, 898

Cyclopropane ring from halides
s. *8*, 930

Spirofluorenes
s. *8*, 931

Potassium hydroxide/toluene

Ethylene derivatives from halides CHCHal → C:
s. *9*, 963

Potassium hydroxide/alcohol

Ethylenehalides
s. *9*, 964

Tolans by rearrangement
s. *7*, 899

Benzene ring from cyclohepta-4,6-diene-1,2-diones ←
Ring contraction
s. *9*, 965

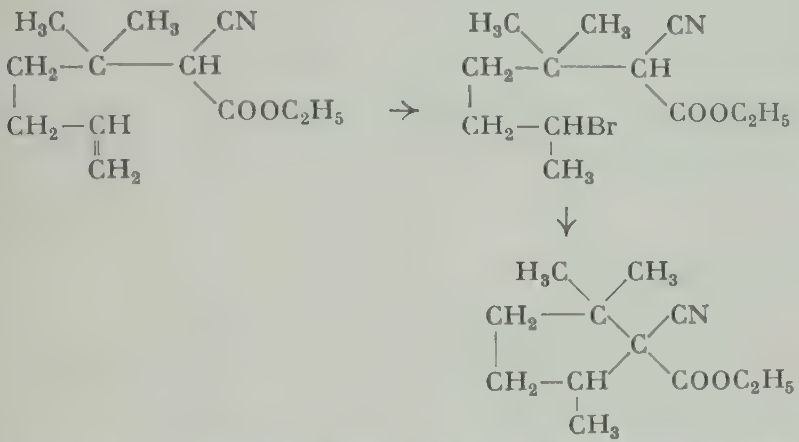
Potassium hydroxide/propyl alcohol

α,β-Ethylenechlorides from 1,2-dichlorides CHClCHCl → CH:CCl
Stereospecificity s. *7*, 738

Sodium/alcohol *NaOR*

Cumulenes from 1,2-ethylene-1,2-dihalides ←
s. *7*, 900

Isocyclics from ethylene derivatives via halides ○



Dry HBr bubbled through a soln. of ethyl 1,1-dimethyl-4-n-pentenylcyanoacetate (prepn. s. 540) in glacial acetic acid and chloroform while keeping the temp. at 5-10° with an ice bath, when the soln. is satd. allowed to warm to room temp. → ethyl 1,1-dimethyl-4-bromo-n-pentylcyanoacetate (Y: 81%) dissolved in abs. ethanol, heated to reflux, a soln. of Na in ethanol added dropwise during 1 hr., and refluxed 4 hrs. → 2,2,5-trimethyl-1-carbethoxy-1-cyanocyclopentane (Y: 75%). F. e. s. E. van Heyningen, Am. Soc. *76*, 2241 (1954).

KOR

Potassium/alcohol C:C·COOH

α,β-Ethylenecarboxylic acids from carboxylic acids via α-bromocarboxylic acids

$n\text{-}C_9H_{19}CH_2CH_2COOH \rightarrow [n\text{-}C_9H_{19}CH_2CHBrCOOH] \rightarrow n\text{-}C_9H_{19}CH{=}CHCOOH$

Crude α-bromo-n-dodecanoic acid, prepared from n-dodecanoic acid and Br_2 in the presence of PCl_3, added to a soln. of 3 equivalents K in *tert*-butanol, and refluxed 4 hrs. → 2-dodecenoic acid. Y: 74%. F. e. s. J. Cason, N. L. Allinger, and G. Sumrell, J. Org. Chem. *18*, 850 (1953).

C_6H_5Li

Phenyllithium

Acetylene derivatives from α,β-ethylenehalides CH:CHal → C⋮C
s. *6*, 880

○

Isocyclics from dihalides
s. *6*, 875; *9*, 966

Lithium amide *LiN*

Acetylene derivatives from α,β-ethylenehalides with subsequent synthesis of acetylenealcohols CH:CHal → C⁝

s. *9*, 736

Sodium amide *NaN*

Acetylene derivatives from 1,2-dihalides CHHalCHHal → C⁝

s. *6*, 878; s. a. H. N. Miller et al., J. Org. Chem. *19*, 1882 (1954); J. H. Allan, E. R. H. Jones, and M. C. Whiting, Soc. *1955*, 1862

Acetyleneamines
Preparation of sodium amide s. *6*, 878

Mild dehydrobromination
s. *6*, 879

Acetylene derivatives from α,β-ethylenehalides CH:CHal → C⁝

from bromides s. *5*, 649; from chlorides in liq. NH_3 s. P. J. Ashworth, G. H. Mansfield, and M. C. Whiting, Org. Synth. *35*, 20 (1955)

Vinylethinyl compounds ←

s. *10*, 517

Polyacetylene derivatives ←

s. *7*, 687

Alkoxyacetylenes from α-halogenacetals $CHHal{\cdot}CH(OR)_2 \rightarrow C{\vdots}C(OR$

681. $ClCH_2CH(OC_2H_5)_2 \rightarrow HC{\equiv}C(OC_2H_5)$

Diethyl chloroacetal added during 15-20 min. with agitation to a suspension of $NaNH_2$ in liq. NH_3, which is then evaporated in a N_2-stream, cooled to −70° under N_2, and a satd. soln. of NaCl cooled to −20° added as rapidly as possible with vigorous agitation → ethoxyacetylene. Y: 61%. F. e. s. G. Eglinton et al., Soc. *1954*, 1860; Org. Synth. *34*, 46 (1954).

Sodium amide/aniline $NaNH_2/C_6H_5NH_2$

Sensitive acetylene derivatives by dehydrohalogenation ←

s. *9*, 967

Sodium hydrogen carbonate $NaHCO_3$

3-Nitropyrazoles from 1-halogeno-1-nitro-1,2-ethylene derivatives ○

s. *8*, 737

Potassium carbonate K_2CO_3

Acetylene derivatives from α,β-dihalogenocarboxylic acids via α,β-ethylenehalides ←

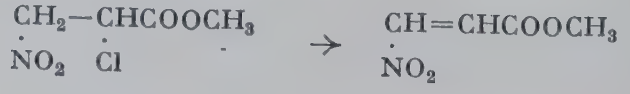
s. *6*, 880

Sodium acetate CH_3COONa

Ethylene derivatives from halides CHCHal → C:C

s. *6*, 891

682.



$$\underset{NO_2}{CH_2}-\underset{Cl}{CH}COOCH_3 \rightarrow \underset{NO_2}{CH}{=}CHCOOCH_3$$

α,β-Nitroethylene derivatives. Methyl 2-chloro-3-nitropropionate added dropwise at 5° to a stirred suspension of Na-acetate in ethyl ether → methyl 3-nitroacrylate. Y: 91.9%. F. e. s. H. Shechter et al., Am. Soc. *74*, 3052 (1952).

Potassium acetate — CH_3COOK
s. *10*, 654

Cyclopropanes from halides — ○
s. *6*, 881; *8*, 932

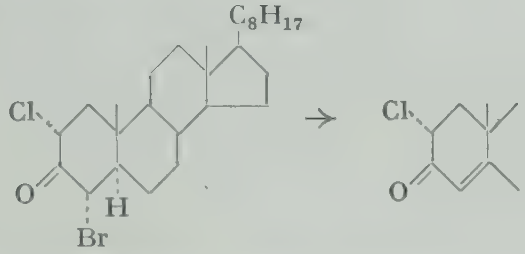
Potassium acetate/phenol s. Phenol/potassium acetate — CH_3COOK/C_6H_5OH

Lithium chloride — *LiCl*

Δ^4-3-Ketosteroids via 4-halogeno-3-ketosteroids — CHCHal → C:C
s. *9*, 968

Sodium iodide — *NaI*

Selective dehydrohalogenation



A soln. of 1.0 g. 2α-chloro-4α-bromocholestan-3-one in methyl ethyl ketone refluxed 10 hrs. with NaI under N_2 → 0.39 g. Δ^4-2-chlorocholesten-3-one. J. J. Beereboom and C. Djerassi, J. Org. Chem. *19*, 1196 (1954).

Ethylene derivatives

from 1,2-dibromides — CBrCBr → C:C
s. *6*, 882

from α-iodo-p-toluenesulfonic acid esters — CIC(OTs) → C:C
s. *8*, 933

Δ^4-3-Ketosteroids – Replacement of bromine by iodine ←

Ethylenehalides from dihalides – Replacement of iodine by hydrogen
s. *7*, 901

Ethylene iodides from 1,2,4-tribromides ←
s. *6*, 882

Ketenimines from α-hydroxycarboxylic acids via α-chlorocarboxylic acid chlorides and amides, and α-chloroiminochlorides — C:C:N·
s. *8*, 934

Diethylamine — $(C_2H_5)_2NH$

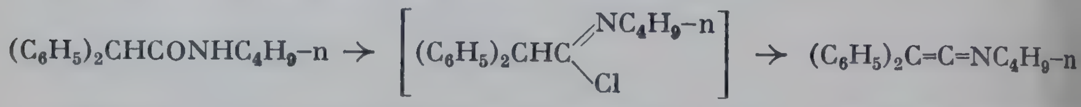
Enamines from 1,2-dibromides — CHBrCHBr → CH:C(N<)
s. *6*, 454

Triethylamine $(C_2H_5)_3N$

Acetylene derivatives from 1,2-dibromides CHBrCHBr → C⋮C
s. *7*, 902

Ketenes from carboxylic acid chlorides CHCOCl → C:C:O
s. *6*, 883

Ketenimines from carboxylic acid amides via iminochlorides C:C:N·

684.

$$(C_6H_5)_2CHCONHC_4H_9\text{-}n \rightarrow \left[(C_6H_5)_2CHC\overset{NC_4H_9\text{-}n}{\underset{Cl}{\lessgtr}}\right] \rightarrow (C_6H_5)_2C{=}C{=}NC_4H_9\text{-}n$$

A mixture of N-(n-butyl)diphenylacetamide, PCl_5, and dry benzene refluxed 90 min., the volatile components then removed in vacuo, the remaining $POCl_3$ removed by co-distillation with benzene, the crude product dissolved in dry ether, triethylamine added, and allowed to stand for 6 hrs. → diphenylketene N-butylimine. Y: 69.2%.—This method appears to be the method of choice for the prepn. of large amounts of ketenimines. However, for those ketenimines which are easily dimerized, the dehalogenation of the α-chloroiminochlorides (cf. Synth. Meth. 8, 934) appears to be the better method. F. e., also isolation of the intermediates, s. C. L. Stevens and J. C. French, Am. Soc. *76*, 4398 (1954).

Furan ring synthesis ○
s. *7*, 814

Azetidinones

Subst. carboxylic acid amides from carboxylic acids
s. *6*, 884

Piperidine $C_5H_{11}N$

α,β-Ethylenenitriles from α-bromonitriles CHCBr → C:C
s. *9*, 899

Aniline/sodium amide s. Sodium amide/aniline $C_6H_5NH_2/NaNH_2$

Diethylaniline $C_6H_5N(C_2H_5)_2$

Dehydrobromination
s. *9*, 619

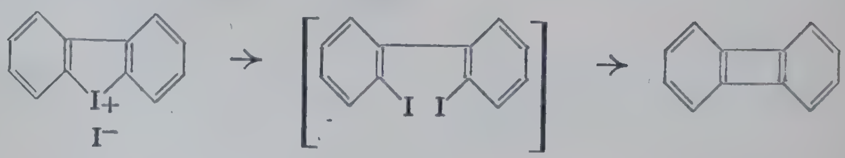
Ring closure to N-heterocyclics ○
s. *9*, 969

Quinoline ←

Ethylene derivatives from halides CHHal → C:C
s. *6*, 840

Cuprous oxide Cu_2O

Isocyclics from iodonium iodides ○

685.


Diphenylenes. A mixture of powdered diphenyl-2,2′-iodonium iodide and Cu_2O heated a few min. at 100°/1 mm., then 4 min. in a metal bath preheated to 350-360° with sublimation of the product → diphenylene (startg. m. f. 74). Y: 28%. W. Baker, M. P. V. Boarland, and J. F. W. McOmie, Soc. *1954*, 1476.

Silver oxide Ag_2O

Ethylene derivatives from bromides CHCBr → C:C

s. *8*, 936

Silver acetate CH_3COOAg

Ethylene derivatives from 1,2-dibromides CBrCBr → C:C

s. *9*, 928

Calcium carbonate $CaCO_3$

Ethylene derivatives from halides CHCHal → C:C

s. *6*, 885

Barium carbonate $BaCO_3$

Ethylenesulfones

s. *6*, 886

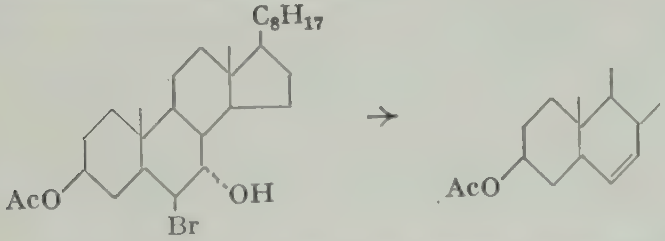
Barium chloride $BaCl_2$

Ethylenecarboxylic acid chlorides

s. *7*, 903

Zinc *Zn*

Ethylene derivatives from halogenhydrins CBrC(OH) → C:C



Ethylenesteroids. 45 mg. 6β-bromo-7α-hydroxycholestan-3β-yl acetate refluxed 3 hrs. with activated Zn (according to L. F. Fieser and W. S. Johnson, Am. Soc. *62*, 576 (1940)) in ethanol → 38 mg. cholest-6-en-3β-yl acetate. F. e. s. D. R. James, R. W. Rees, and C. W. Shoppee, Soc. *1955*, 1370.

Glycals from acetobromosugars CBrC(OAc) → C:C

s. *6*, 887

Ethylene derivatives from 1,2-dibromides CBrCBr → C:C

s. *6*, 280; *9*, 362

Partial and selective dehalogenation of polyhalides

s. *7*, 904; s. a. R. N. Haszeldine and J. E. Osborne, Soc. *1955*, 3880

Acetylenehalides CBr:CBr → C⋮C

s. *9*, 970

Ethylene derivatives from halogenamines CHalC (N<) → C
s. *8*, 937

Ketenes from α-halogenocarboxylic acid halides CHalCOHal → C:C:
s. *9*, 960

Cyclopropane ring
s. *3*, 756; s. a. Y. M. Slobodin, V. I. Grigor'eva, and Y. E. Shmuly kovskiĭ, Ж. *23*, 1665 (1953); C. A. *48*, 13637g; R. G. Kelso et al., Am Soc. *77*, 1751 (1955)

Zinc/sodium iodide *Zn/Na*

Ethylene derivatives from 1,2-dibromides CBrCBr → C:
s. *9*, 603

Zinc/acetic acid Zn/CH_3COOH

s. *9*, 97; with simultaneous hydrogenation of carbon-carbon double bonds s. *8*, 938

Zinc/hexachloroplatinic acid Zn/H_2PtCl_6

Glycals from acetobromosugars CBrC(OAc) → C:C
s. *6*, 888

Lithium aluminum hydride $LiAlH_4$

2-Ethylenealcohols from α,β-dibromocarboxylic acid esters CBr·CBr·COOR → C:C·CH_2OH

687. $CF_3CHBrCHBrCOOC_2H_5 \rightarrow CF_3CH{=}CHCH_2OH$

An ethereal soln. of ethyl 2,3-dibromo-4,4,4-trifluorobutyrate added dropwise at −80° during 2 hrs. to a soln. of $LiAlH_4$ in dry ether, stirring continued 20 hrs. at ca. −80°, then excess $LiAlH_4$ destroyed with 95%-ethanol → 4,4,4-trifluorocrotyl alcohol. Y: 50%. E. T. McBee, O. R. Pierce, and D. D. Smith, Am. Soc. *76*, 3725 (1954).

Aluminum chloride $AlCl_3$

Cyclic ketones from carboxylic acid chlorides ○
s. *6*, 861

Ruggli-Ziegler dilution principle
s. *9*, 971; 1,2,3,4-benzocyclo-1,3-dien-5-ones s. A. *586*, 52 (1954)

3,4-Dihydroisoquinolines via iminochlorides
s. *8*, 939

Naphtho[1,8-bc]thiapyrans
s. *6*, 889

Aluminum bromide $AlBr_3$

Cyclic ketocarboxylic acid esters from dicarboxylic acid chloride esters
s. *8*, 941

Trimethylene glycol $OH[CH_2]_3OH$

Dehydrogenation via 1,2-dibromides CBrCBr → C:C
s. *9*, 972

Amberlite ←

Aromatization CHCCl → C:C
s. *9*, 973

Phenol/potassium acetate *C_6H_5OH/CH_3COOK*

Ethylenechlorides from dichlorides with rearrangement ←
s. *8*, 940

Acetic acid *CH_3COOH*

Mattox-Kendall reaction CH·CHal·CO → C:C·C:N·NHR
α,β-Ethylenehydrazones from α-halogenoketones
s. *9*, 974

Allyl bromide *$CH_2{:}CHCH_2Br$*

Ethylene derivatives from bromides CHCBr → C:C
s. *9*, 927

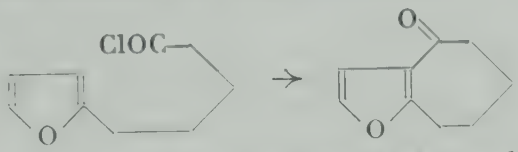
Stannous chloride *$SnCl_2$*

Aromatization ←
s. *7*, 905

Stannic chloride *$SnCl_4$*

Cyclic ketones from carboxylic acids ○
s. *7*, 325

Cyclic ketones from carboxylic acid chlorides



Acid sensitive compounds. A soln. of furylvaleric chloride in CS_2 and a soln. of $SnCl_4$ in the same solvent added dropwise and simultaneously with stirring during 2 hrs. to refluxing CS_2, refluxing and stirring continued for 1 hr. → furocyloheptenone. Y: 60%.—This procedure avoids tar formation by the resulting HCl (cf. 628). W. Treibs and W. Heyer, B. 87, 1197 (1954).

Cyclic ketocarboxylic acid esters
from dicarboxylic acid chloride esters,
with and without ester exchange
s. *8*, 941

Sulfuric acid *H_2SO_4*

N-Heterocyclics from halogenocarboxylic acid amides
Oxindoles s. *9*, 975

Bicyclo[3.3.0]octane ring from cyclooctane ring ←
s. *6*, 890

Via intermediates *v.i.*

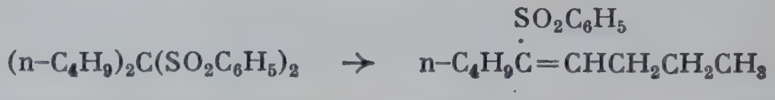
α,β-Ethyleneketones from α-halogenoketones CHCHal → C:C
via α,β-ethylenehydrazones
Mattox-Kendall reaction – Modified procedure
Deutero compounds s. *6*, 891

Sulfur ↑

Without additional reagents

α,β-Ethylenesulfones from 1,1-disulfones

689.



$$(n\text{-}C_4H_9)_2C(SO_2C_6H_5)_2 \rightarrow n\text{-}C_4H_9\overset{SO_2C_6H_5}{C}=CHCH_2CH_2CH_3$$

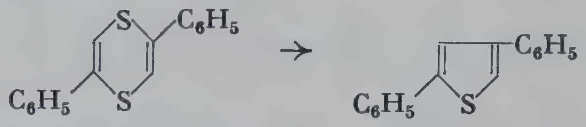
5,5-Bis(phenylsulfonyl)nonane heated at 20 mm. pressure, whe decomposition and distillation occur at 200-250°, the product tre with charcoal in ether, then with Raney-Ni in ethanol → 5-phe sulfonyl-4-nonene. Y: 96%. F. e. s. M. W. Cronyn and E. Zavari Org. Chem. *19*, 139 (1954).

7-Bicyclo[2.2.2]octene-2,3,5,6-tetracarboxylic acid anhydrides from thiophene 1,1-dioxides

s. *9*, 976

Thiophenes from 1,4-dithiins

690.



2,5-Diphenyl-1,4-dithiadiene heated under N_2 at 200° oil bath te until after 2 min. a vigorous reaction occurs raising the temp. of melt from 190 to 250° → 2,4-diphenylthiophene. Y: 69%. W. E. Parh and V. J. Traynelis, Am. Soc. *76*, 4960 (1954); cf. Am. Soc. *77*, (1955).

Sodium hydroxide

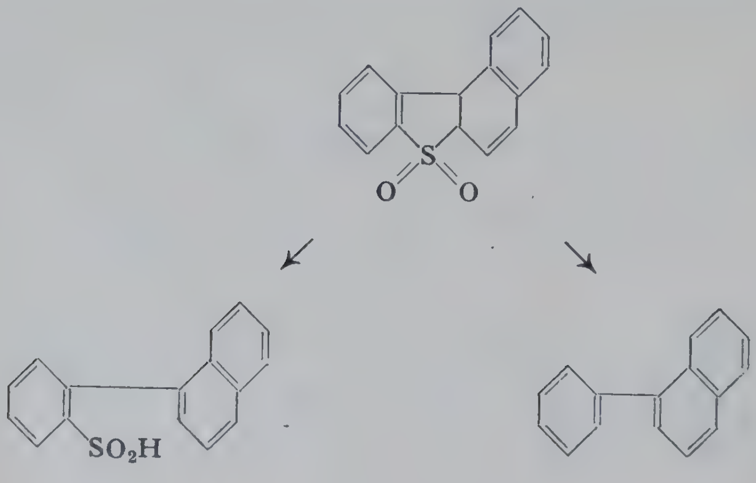
Ethylene derivatives from α-halogenosulfones

s. *8*, 942

Potassium hydroxide

Sulfinic acids and hydrocarbons from cyclic sulfones

691.



Equal weights of 10,11-dihydro-9-thia-3,4-benzofluorene 1,1-dioxide (prepn. s. 632) and powdered KOH

very carefully heated until fusion just occurs → 1-o-sulfinophenylnaphthalene. Y: 92%.

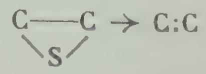
fused and heated until no more liquid distils → 1-phenylnaphthalene. Y: 79%.

W. Davies, N. W. Gamble, and W. E. Savige, Soc. *1952*, 4678.

n-Butyllithium *n-C₄H₉Li*

Ethylene derivatives from ethylene sulfides

s. *9*, 689



Copper *Cu*

Stilbenes from s-trithianes ⊂

s. *9*, 677

Lead acetate *$(CH_3COO)_2Pb$*

Ethylene derivatives and mercaptans from thioethers CHC(SR) → C:C

s. *9*, 655

Remaining Elements CC ⇑ Rem

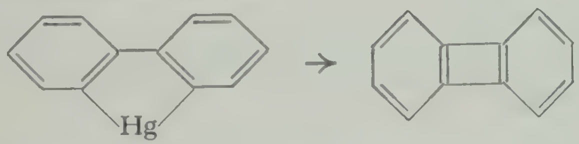
Without additional reagents *w.a.r.*

Photoreactions of organomercury compounds ←

s. *6*, 892

Silver *Ag*

Isocyclics from Hg-heterocyclics ←



Diphenylenes. A mixture of diphenylenemercury and Ag-powder heated several hrs. at 290-300° with sublimation of the product → diphenylene. Y: 54%. G. Wittig and W. Herwig, B. *87*, 1511 (1954).

Aluminum chloride *$AlCl_3$*

Cyclopropanes from 1,3-halogenosilanes ○

γ-Elimination

s. *6*, 893

Carbon ↑ CC ⇑ C

Without additional reagents *w.a.r.*

Thermal decomposition of subst. 9,10-dihydroanthracenes ←

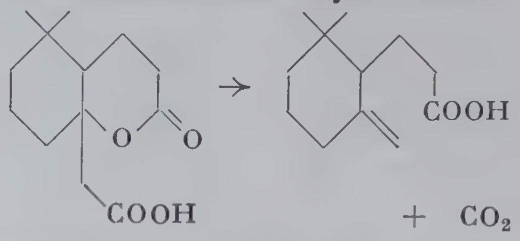
s. *9*, 977

Aromatization via dimers ←

s. *8*, 948

Ethylenecarboxylic acids from carboxylactones

693.



Carboxylactone heated a short time at 200°, then distilled in a h vacuum at 160-170° → 1,1-dimethyl-2-(β-carboxyethyl)-3-methyle cyclohexane. Y: ca. 100%. D. Stauffacher and H. Schinz, Helv. 1227 (1954); f. e. s. Helv. *37*, 957.

Sodium hydroxide *Na*

Methyl ketones from β-halogeno-α-keto-γ-lactones via acetylenecarboxylic acids

s. *7*, 906

Cyclic ketones from o-quinones Elimination of carbon monoxide – Ring contraction

s. *7*, 907

Sodium hydroxide/potassium hydroxide *NaOH/K*

Ethylene derivatives by C-elimination

s. *9*, 978

Potassium hydroxide *K*

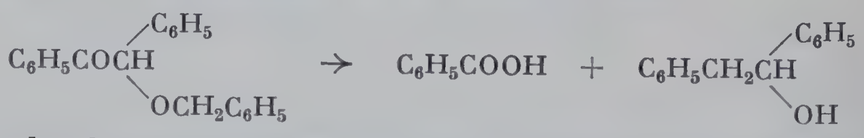
Benzene ring from cyclohepta-4,6-diene-1,2-diones

s. *9*, 965

Potassium hydroxide/alcohol

Cleavage and rearrangement of ethers with bases

694.



$$C_6H_5CO\overset{C_6H_5}{\underset{OCH_2C_6H_5}{CH}} \rightarrow C_6H_5COOH + C_6H_5CH_2\overset{C_6H_5}{\underset{OH}{CH}}$$

Benzyl desyl ether refluxed 25 min. with methanolic 25%-KOH - benzylphenylcarbinol (Y: 84%) and benzoic acid (Y: 91%). F. e. ar limitations s. D. Y. Curtin and W. R. Proops, Am. Soc. *76*, 494 (1954

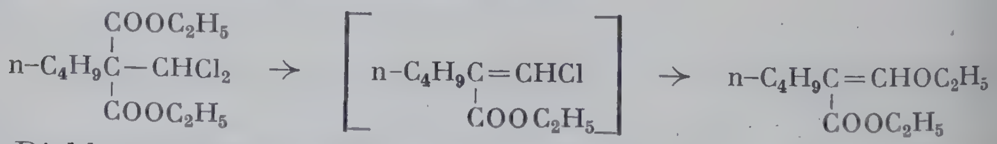
Benzofurans

s. *7*, 688

Sodium alkoxide *Na*

α-Alkoxymethylenecarboxylic acid esters from dichloromethylmalonic acid esters

695.



$$n\text{-}C_4H_9\overset{COOC_2H_5}{\underset{COOC_2H_5}{C}}-CHCl_2 \rightarrow \left[n\text{-}C_4H_9\underset{COOC_2H_5}{C}=CHCl\right] \rightarrow n\text{-}C_4H_9\underset{COOC_2H_5}{C}=CHOC_2H_5$$

1,1-Dichloro-2,2-dicarbethoxyhexane added to a suspension of 2 mole Na-ethoxide in xylene (prepared by dissolving Na in a mixture of eth nol and xylene, then removing the excess ethanol by distillation), and refluxed 15 min. → 1-ethoxy-2-carbethoxy-1-hexene. Y: 93.4%.—By using 1 equivalent ethoxide, α-chloromethylenecarboxylic acid esters are obtained in yields generally over 90%. F. e. s. N. B. Bowman and D. R. Rexford, J. Org. Chem. *19*, 1219 (1954).

Phenyllithium *C_6H_5Li*

Isoindoles ←

s. *7*, 908; cf. A. *548*, 1 (1953)

Sodium amide/potassium hydroxide *$NaNH_2/KOH$*

Isatins and indigo compounds ○

s. *6*, 895

Alkali hydrogen carbonate ←

α-Halogen-α,β-ethylene-ketones and -carboxylic acid esters from β-halogeno-α-keto-γ-lactones ↻

s. *8*, 943

Sodium carbonate *Na_2CO_3*

Indenones from phthalides ←

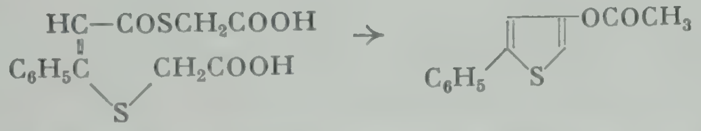
s. *7*, 909

Sodium acetate *CH_3COONa*

Benzofurans with simultaneous decarboxylation ○

s. *6*, 896

Thiophenes



A mixture of *cis*-4-keto-6-phenyl-3,7-dithia-5-nonenedioic acid and anhydrous Na-acetate heated 4 hrs. in acetic anhydride on a water bath → 5-phenyl-3-acetoxythiophene. Y: 90%. A. I. Kosak et al., Am. Soc. *76*, 4450 (1954); method s. F. Friedlaender and S. Kielbasinski, B. *45*, 3389 (1912).

Sodium iodide *NaI*

Ethylene derivatives from lactones ↻

s. *6*, 897

Alkali salt ←

Ethylene derivatives from salts of halogenocarboxylic acids ←

Degradation with loss of 1 C-atom

s. *8*, 944; also fluorocarbon monohydrides in ethylene glycol s. Am. Soc. *75*, 4525 (1953); s. a. J. D. Lazerte and R. J. Koshar, Am. Soc. *77*, 910 (1955); 1.2-dichlorodifluoroethylene s. R. N. Haszeldine and J. E. Osborne, Soc. *1955*, 3880.

Silver oxide A

Hydrocarbons from carboxylic acid anhydrides by dimerization
s. *8*, 873

Cupric acetate $(CH_3COO)_2$

α-Diketones from 1,2,3-triketones RCOCOCOR → RCOC
s. *7*, 910

Cuprous cyanide Cu

Acylcyanides and ethylene derivatives from carboxylic acid halides
s. *6*, 898

Barium hydroxide/iron $Ba(OH)_2/$

Cyclic ketones from dicarboxylic acids
s. *4*, 857; s. a. Coll. Czech. Chem. Communs. *19*, 1264 (1954)

Aluminum chloride Al

Cyclic aminoketones from N-carboxyaminocarboxylic acid anhydrides
s. *6*, 829

Diene C:C·C

Dissociation of Diels-Alder adducts
s. *7*, 911

Acetic anhydride $(CH_3CO)_2$

Cyclic ketones from dicarboxylic acids according to Blanc
s. *6*, 899

Lead carbonate PbC

Ring contraction of isocyclics
Cyclic ketones from dicarboxylic acids
s. *8*, 945

Lead tetraacetate $(CH_3COO)_4P$

Carboxylic acids from α-ketocarboxylic acids RCOCOOH → RCOO
s. *9*, 347

Hydrogen peroxide H_2O
s. *6*, 747

Sulfur

Aromatization
s. *6*, 900

Potassium hydrogen sulfate KHSO

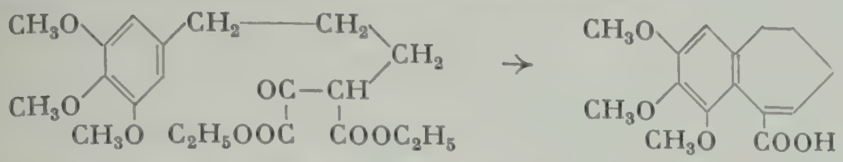
Cleavage of di-tert-1,3-diols
s. *9*, 979

Sulfuric acid H_2SO

α,β-Ethylenealdehydes from α-alkoxymethyleneketones
s. *7*, 118

α,β-Ethyleneketones from 3-alkoxy-2-ethylenealcohols
s. *9*, 980

Ring closure to isocyclics with simultaneous decarboxylation and hydrolysis ○



A mixture of ethyl α-ethoxalyl-δ-(3,4,5-trimethoxyphenyl)valerate and 16%-H_2SO_4 refluxed 5 hrs. with stirring → 2,3,4-trimethoxybenzosuber-5-ene-5-carboxylic acid. Y: 86-91%. J. Koo and L. Hartwell, Am. Soc. 75, 1625 (1953).

Selenium *Se*

Elimination of nonangular alkyl groups in aromatization reactions ←

s. 8, 946

Chromium oxide-alumina *Cr_2O_3-Al_2O_3*

Synthesis of alkylbenzenes
Dehydration and aromatization ←

s. 9, 981

Hydrochloric acid *HCl*

Cyclohexanone ring via β-ketoenollactones ←
Introduction of isotopic carbon into ring A of steroids

s. 7, 912

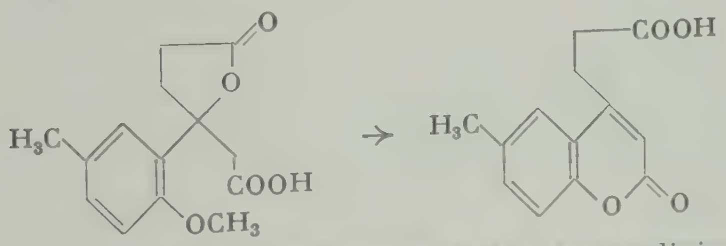
Hydrobromic acid *HBr*

Cyclic ketones from polycarboxylic acids ○

s. 9, 982

Hydriodic acid *HI*

Coumarin ring



A soln. of β-(2-methoxy-5-methylphenyl)-β-hydroxyadipic acid γ-lactone in 47%-HI and glacial acetic acid refluxed 2 hrs. → β-(6-methyl-4-coumarin)propionic acid. Y: 72%. F. e. s. A. S. Dreiding and A. J. Tomasewski, Am. Soc. 76, 540 (1954).

Manganous carbonate *$MnCO_3$*

Cyclic ketones from dicarboxylic acids

s. 8, 947

Iron/barium hydroxide s. Barium hydroxide/iron *Fe/Ba$(OH)_2$*

Palladium-carbon *Pd-*

Aromatization ←
s. *9*, 983

Via intermediates *v.*

Desoxybenzoins from chalcones ←
via α,β-oxidoketones and α-hydroxycarboxylic acids
s. *6*, 901

Aromatization via dimers – Steroids with an ar. B ring ←
s. *8*, 948

Formation of Electron Pair on Nitrogen

Elimination

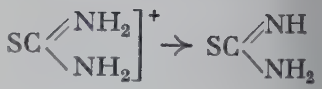
Hydrogen ↑ ElN ⇑ H

Without additional reagents *w.a.r.*

Organo boron compounds ←
s. *8*, 949

Sodium hydroxide *NaOH*

Isothioureas from isothiouronium salts
s. *8*, 950



$$\left[SC\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}\right]^+ \rightarrow SC\begin{matrix}\diagup\!\!\diagup NH\\ \diagdown NH_2\end{matrix}$$

Betaine azeniates ←
s. *6*, 902

Aminesulfonimides from sulfonylhydrazonium salts and reverse reaction ←
s. *9*, 984

Potassium hydroxide *KOH*

Bases from their hydrochlorides ←

C-Aminosilanes
s. *9*, 985

Sodium/alcohol *NaOR*

Peptide esters
s. *8*, 230

Ammonia *NH_3*

Aminocarboxylic acid esters s. *5*, 663; aminosteroids s. R. A. Micheli and C. K. Bradsher, Am. Soc. *77*, 4788 (1955)

Alkylamines ←

s. *6*, 903; with dicyclohexylamine s. F. Weygand and M. Reiher, B. *88*, 26 (1955)

Anion exchange resin

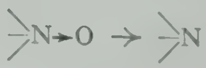
Aminocarboxylic acids with Amberlite s. *8*, 171; aminoalcohols with Permutit S-1 s. L. Berlinguet, Can. J. Chem. *32*, 31 (1954) ←

Bases from their picrates
s. *7*, 913 ←

Oxygen ↑ ElN ⇑ O

Aniline $C_6H_5NH_2$

Reduction of N-oxides
s. *9*, 986

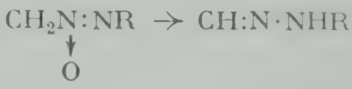


Zinc and lithium aluminum hydride *Zn and* $LiAlH_4$

Cinnolines from cinnoline N-oxides
s. *8*, 951

Lithium aluminum hydride $LiAlH_4$

Hydrazones from azoxy compounds
s. *9*, 167



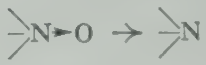
$CH_2N(\rightarrow O){:}NR \rightarrow CH{:}N{\cdot}NHR$

Carbon monoxide CO

High pressure reductions with carbon monoxide ←
Azo compounds from azoxy compounds
s. *6*, 904

Peracetic acid CH_3COO_2H

Reduction of N-oxides



Deoxygenations in the presence of oxidizing agents
s. *8*, 136

Sulfur dioxide SO_2

Amines from N-oxides
s. *8*, 952

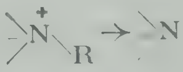
Iron Fe

with simultaneous formation of amines from nitro compounds
s. *6*, 389

Carbon ↑ ElN ⇑ C

Without additional reagents *w.a.r.*

Tert. amines from quaternary ammonium salts
s. *9*, 418; piperazines s. J. I. G. Cadogan, Soc. *1955*, 2971

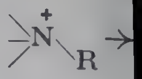


Sodium hydroxide $NaOH$

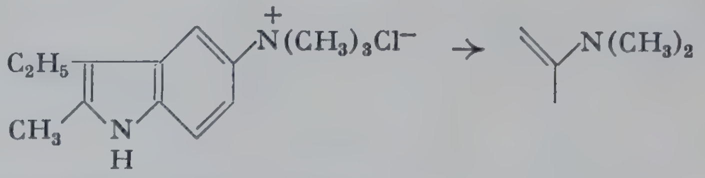
Tert. amines from betaines ←
s. *9*, 217

Sodium/alcohol *Na*

Tert amines from quaternary ammonium salts



699.



(2-Methyl-3-ethylindolyl-5)-trimethylammonium chloride refluxed hrs. with a soln. of excess Na in n-propanol → 2-methyl-3-ethyl-5 methylaminoindole. Y: 80%. F. e. s. E. Shaw, Am. Soc. *76*, 1384 (195

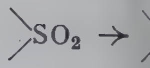
Formation of Electron Pair on Sulfur

Elimination

Oxygen ↑ ElS ⇑

Zinc/hydrochloric acid *Zn/H*

Thiophenes from thiophene 1,1-dioxides
s. *9*, 987



Lithium aluminum hydride *LiAl*

Thioethers from sulfones
s. *7*, 914; in diethyl ether s. S. F. Birch et al., J. Org. Chem. *20*, 11 (1955)

Sym. disulfides from thiosulfonic acid esters $2\ R \cdot SO_2SR \rightarrow R \cdot SS$
s. *6*, 47

Formation of Electron Pair on Remaining Elements

Elimination

Halogen ElRem ⇑ H

Stannous chloride *SnC*

Antimony(III) from antimony(V) compounds
s. *6*, 905

Phosphorus

Phosphinous chlorides from dithiophosphinic acids via phosphoranetrioic trichlorides

700. $(C_6H_5)_2PSSH \rightarrow (C_6H_5)_2PCl_3 \rightarrow (C_6H_5)_2PCl$

Cl-gas passed at 25-50° into a stirred soln. of crude diphenylphosphin dithioic acid in benzene for 4 hrs., petroleum ether (b. p. 80-100°) ad ed, the precipitate allowed to settle for 1 hr., the supernatant liquid siphoned off, the residue washed with petroleum ether to remove S_2Cl_2. te crystalline mush of crude diphenylphosphoranetrioic trichloride containing petroleum ether treated with red P, stirred and heated slowly to 180° with distillation of PCl_3 and petroleum ether → diphenylphosphinous chloride. Y: 72%. Reactions s. C. Stuebe, W. M. LeSuer, and G. R. Norman, Am. Soc. 77, 3526 (1955).

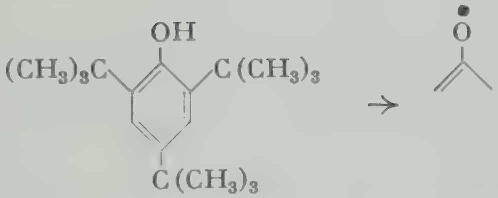
Oxygen Radicals

Elimination

Hydrogen ↑ **RadO ⇑ H**

Potassium ferricyanide *$K_3[Fe(CN)_6]$*

Aroxyls ←



K-ferricyanide and KOH in water and benzene stirred 1.5 hrs. while flushing with N_2, then 2.4,6-tri-*tert*-butylphenol added, and the mixture stirred slowly for 2 hrs. at room temp. → benzene soln. of 2.4.6-tri-*tert*-butylphenoxyl. Y: 99-100%. C. D. Cook and R. C. Woodworth, Am. Soc. 75, 6242 (1953).

Nitrogen Radicals

Elimination

Hydrogen ↑ **RadN ⇑ H**

Lead dioxide *PbO_2*

Oxyhydrazyl radicals from hydrazines
via hydrazyl radicals and hydroxyhydrazines ←
s. *9*, 988

Halogen ↑ **RadN ⇑ Hal**

Sodium stannite *Na_2SnO_2*

Tetrazolium radicals ←
s. *9*, 989

Heteropolar Bond

Uptake

Addition to Oxygen Het

Without additional reagents *u*

Trialkyl- via dialkyl-oxonium salts
s. *9*, 990; s. a. B. *86*, 1322 (1953)

Addition to Nitrogen Het

Without additional reagents *w*

Resolution of stereoisomers via salts
s. *5*, 666; *7*, 915; s. a. L. Velluz, Bl. *1953*, 904; J. Rudinger and H. Cz
bová, Coll. Czech. Chem. Communs. *19*, 386 (1954)

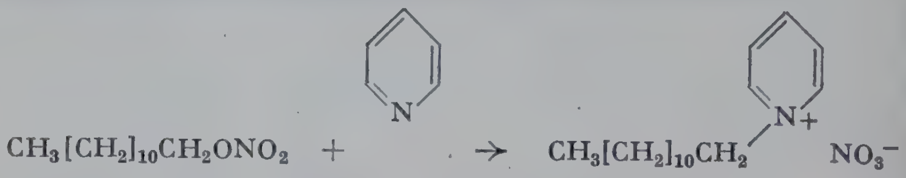
Quaternary ammonium salts
s. *6*, 906

from tert. amines
s. *7*, 811, 916; *9*, 991

from dibromides
s. *6*, 907; mono-salts s. A. P. Gray et al., Am. Soc. *77*, 3648 (19

Quaternary ammonium nitrates from nitric acid esters

702.

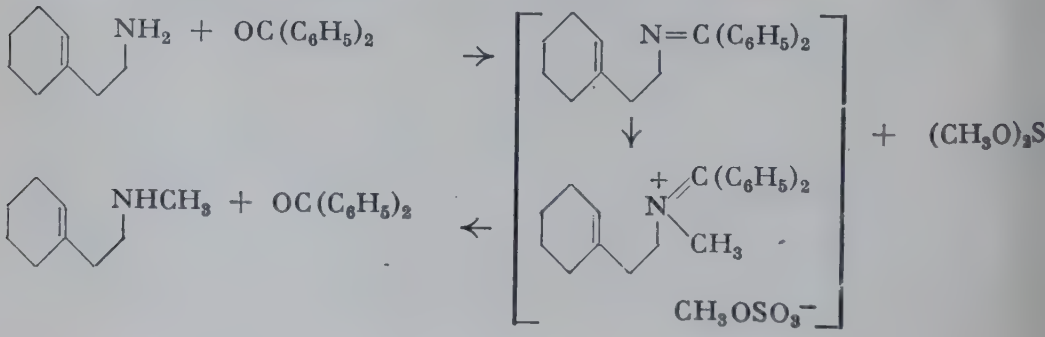


100 g. dodecyl nitrate and 52 g. pyridine refluxed 24 hrs. → 98 g.
decylpyridinium nitrate. F. e. s. E. S. Lane, Soc. *1953*, 1172.

Alkyl sulfates s. *6*, 908	**Methosulfates** s. *6*, 820
Methiodides s. *7*, 640	**Pyridinium salts** s. *10*, 79

Sec. from prim. amines via azomethinium salts $NH_2 \rightarrow NH$

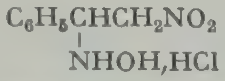
703.



Azeotropic water separation. Cyclohexenylethylamine and benzophenone refluxed in xylene in the presence of a complex salt prepared from the same amine and Zn-chloride, $[Zn(RNH_2)_2]Cl_2$, until after ca. 4 hrs. the calculated amount of water has been separated, cooled, the amine-$ZnCl_2$ complex salt removed by filtration, the filtrate containing the Schiff base (Y: 94% when isolated) treated with dimethyl sulfate, heated 1 hr. on a steam bath whereby the quaternary salt precipitates, extracted with 2 *N* HCl, made alkaline whereby cleavage occurs, and reacidified after some time → N-methylcyclohexenylethylamine. Y: 86%.—Benzophenone is recovered quantitatively. R. Grewe et al., A. *581*, 85 (1953); method of azomethine formation s. G. Reddelien, B. *43*, 2476 (1910); cf. J. Harley-Mason and A. H. Jackson, Soc. *1954*, 3651.

Hydroxylammonium salts ←

4.



$$C_6H_5\underset{\displaystyle NHOH,HCl}{\underset{|}{C}}HCH_2NO_2$$

N-(1-Phenyl-2-nitroethyl)hydroxylamine (prepn. s. 276) dissolved in a minimum of anhydrous dioxane, abs. ether added to the cloud point, satd. with anhydrous HCl, and the product precipitated by addition of anhydrous ether → N-(1-phenyl-2-nitroethyl)hydroxylammonium chloride. Y: 99.2%. C. D. Hurd and J. Patterson, Am. Soc. *75*, 285 (1953).

Sodium nitrite *$NaNO_2$*

Ammonium salts – Nitrites ←

s. *8*, 953

Ammonium salt *NH_4^+*

Resolution of stereoisomers via d-α-bromocamphor-π-sulfonates ←

s. *7*, 917

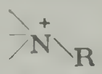
Acetic anhydride *$(CH_3CO)_2O$*

Hydrazone perchlorates ←

s. *8*, 954

Acetic acid *CH_3COOH*

Pure quaternary ammonium salts from tert. amines



Methosulfates s. *9*, 992

Triphenyl phosphite methiodide *$(C_6H_5O)_3PCH_3I$*

Quaternary ammonium salts from alcohols

s. *9*, 993

Via intermediates *v.i.*

Acridinium salts

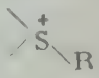
s. *6*, 909

Het ⇓ S

Addition to Sulfur

Without additional reagents *w.a.r.*

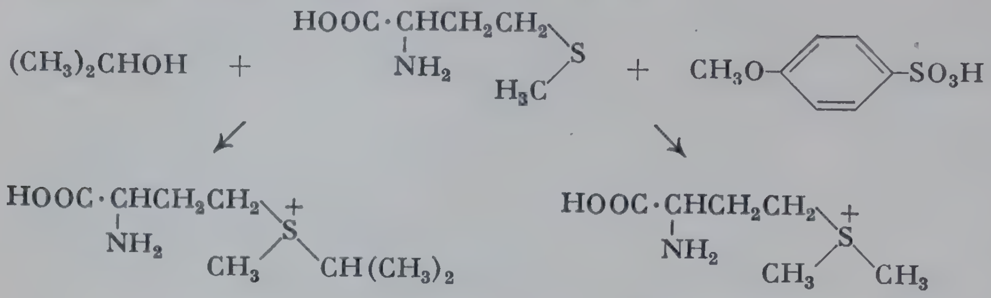
Sulfonium salts



s. *6*, 910; *8*, 955; with simultaneous formation of ketals s. *6*, 212

Sulfonium salts from alcohols and ethers

705.



A mixture of DL-methionine, ca. 50%-H_2SO_4, and

isopropanol heated 1 hr. at 135°, and the product isolated as the bromide via the phosphotungstate → DL-methionine isopropylsulfonium bromide. Y: 68%.	p-methoxyphenylsulfonic acid refluxed 2 hrs., and the product isolated as the phosphotungstate → DL-methionine methylsulfonium phosphotungstate. Y: 90%.

F. e. s. T. F. Lavine, N. F. Floyd, and M. S. Cammaroti, J. Biol. Chem. *207*, 107 (1954).

Addition to Sulfur and Carbon

Het ⇓ SC

Without additional reagents

w.a.r.

2-Alkylmercaptothiazolinium salts from 4-thiazolidone-2-thiones

←

s. *7*, 305

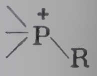
Addition to Remaining Elements

Het ⇓ Rem

Without additional reagents

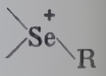
w.a.r.

Phosphonium salts

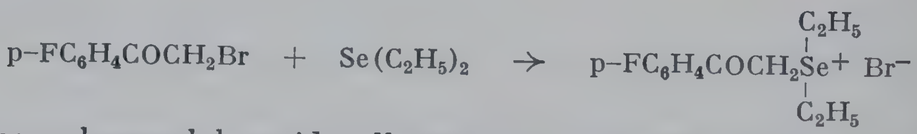


s. *6*, 911; in benzene at room temp. s. F. Bohlmann and H.-J. Mannhardt, B. *88*, 1330 (1955)

Selenonium salts



706.



$$p\text{-}FC_6H_4COCH_2Br + Se(C_2H_5)_2 \rightarrow p\text{-}FC_6H_4COCH_2\overset{C_2H_5}{\underset{C_2H_5}{Se}}{}^{+}\ Br^-$$

p-Fluorophenacyl bromide allowed to react with a slight excess of diethyl selenide at room temp. for 5 min. → Crude p-fluorophenacyl diethyl selenonium bromide. Y: 85%. F. e. s. C.T. Bahner, P.P. Neblett, Jr., and H. A. Rutter, Jr., Am. Soc. *74*, 3453 (1952).

Exchange

Het ⇅

Without additional reagents

w.a.r.

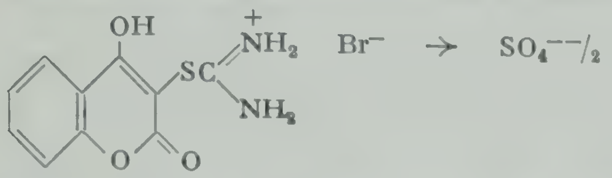
Xanthylium salts from xanthydrols

←

s. *7*, 918

Organobismuth(V) compounds ←
s. *8*, 956

Isothiouronium sulfates from isothiouronium halides ←



3-Isothiourea-4-hydroxycoumarin hydrobromide added in small portions at room temp. to concd. H_2SO_4, then poured with stirring into ice-water → di-(3-isothiourea-4-hydroxycoumarin) sulfate. Y: 93%. H. R. Eisenhauer and K. P. Link, Am. Soc. *76*, 1647 (1954).

Silver oxide *Ag_2O*

Silver salts from carboxylic acids COOH → COOAg
s. *8*, 629

Exchange of anions of quaternary ammonium salts ←
Iodides from chlorides s. *8*, 84; bromides from iodides s. W. F. Cockburn and A. F. McKay, Am. Soc. *77*, 397 (1955)

Silver sulfate *Ag_2SO_4*

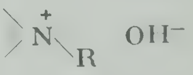
Sulfates from iodides
s. *7*, 919

Silver chloride *AgCl*

Chlorides from iodides
s. *9*, 949; methochlorides s. *6*, 724, 906

Thallous hydroxide *TlOH*

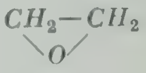
Quaternary ammonium hydroxides
s. *8*, 917



Methyl alcohol *CH_3OH*

Organic ammonium chlorides from bromides and iodides ←
s. *8*, 957

Ethylene oxide



$\underset{\diagdown O \diagup}{CH_2-CH_2}$

Exchange of anions of quaternary ammonium salts
s. *9*, 994

Amberlite ←

Bromides from methanesulfonates
s. *9*, 430

Acids from their salts ←
s. *6*, 912

Dowex-50
s. *10*, 405

Acetic acid/urea *$CH_3COOH/CO(NH_2)_2$*

Aliphatic nitro compounds from nitronates ←
s. *8*, 958

Salicylic acid ←
s. 8, 959

2,4-Diguanidinophenyl lauryl ether ←
Chlorides from picrates of sensitive bases ←
s. 9, 995

Elimination

Carbon ↑ Het ⇑

Sodium hydrogen carbonate *NaHCO*
Inner isothiouronium salts ←
s. 8, 653

Other Reactions Oth

Without additional reagents *w.a.r.*
Pyridinium bromide perbromides ←
s. 8, 586

Acetone CH_3COCH_3
Pyridinium bromides from pyridinium bromide perbromides ←
s. 8, 586

Cumulative Index

Volumes 6–10

(Cumulative Index, Volumes 1–5, see Volume 5, page 503)

The subject index lists the names of the methods, types of compounds, reagents, etc. For specific compounds and for authors (when a method is not named after them) the reader may be referred to the indexes of abstract journals. Complex compounds, as those with several functional groups, are referred to under the related simpler compounds, under *special s.* E.g. aminocarboxylic acids are found under carboxylic acids. Only compounds beginning with letters other than those of the parent or main compounds are listed under this subentry, and entry numbers are omitted because they are specified when the compound is given as a main entry. Derivatives used for characterization, identification, or separation are listed under the subentry *derivatives.* Methods of synthesis for a given substance are indexed under the name of this substance and the subentry *from*, e.g. carboxylic acids from alcohols, hydrocarbons. Syntheses carried out from a particular starting material are indexed under the starting material and the subentry *startg. m. f.* (starting material for the preparation of . . .), e.g. alcohols, startg. m. f. carboxylic acids, ketones.

Classes of compounds may be designated merely by the functional group that is changed during the reaction. Ring compounds may also refer to the corresponding hydrogenated rings, unless the latter are listed specifically. If that be the case, then, as in several other cases, the *inversion* has been made use of that is customary in the indexes of Chemical Abstracts. Dihydrofurans, e.g., may be found under Furans, dihydro-. All single letters, which are separated from the name by a hyphen, are being ignored in regard to alphabetic arrangement, e.g., 'O-Acetyl derivatives' are listed under A.

Generalregister

Band 6–10

(Generalregister Band 1–5 siehe Band 5, Seite 503)

Im alphabetischen Register finden sich als Schlagworte Methoden, Verbindungsklassen, Reagenzien u. dgl.; Einzelverbindungen und Autoren, soweit nicht eine Methode nach ihnen benannt ist, sind, wie bisher, in den Registern der Referatenblätter zu suchen. Auf kompliziertere Verbindungen, z. B. mit mehreren funktionellen Gruppen, ist

bei den entsprechenden einfacheren Verbindungen unter *special s.* (spezielle siehe) hingewiesen, z. B. bei Carbonsäuren auf Aminocarbonsäuren. Es wird hier jedoch nur auf Verbindungen hingewiesen, die einen anderen Wortanfang haben und deshalb an anderer Stelle im Register stehen. Derivate, die zur Charakterisierung, Identifizierung, oder Trennung dienen, sind unter *derivatives* aufgeführt. Methoden zur Synthese eines bestimmten Endprodukts findet man beim Schlagwort dieses Endprodukts unter *from* (aus) registriert, z. B. Carbonsäuren aus Alkoholen, Kohlenwasserstoffen. Synthesen, die sich mit einem bestimmten Ausgangsmaterial ausführen lassen, sind bei dem Schlagwort des Ausgangsmaterials unter *startg. m. f.* (Ausgangsmaterial für die Darstellung von ...) zu suchen, z. B. Alkohole, Ausg. f. Ketone, Carbonsäuren.

Die Bezeichnung der Verbindungsklassen kann sich auf funktionelle Gruppen beschränken, die bei der Reaktion verändert werden. Ringbezeichnungen können sich auch auf die entsprechenden hydrierten Ringe beziehen. Sind hydrierte Ringe aber besonders aufgeführt, dann ist bei ihnen, wie auch in einigen anderen Fällen, von der Inversion Gebrauch gemacht worden, wie sie in den Sachregistern der «Chemical Abstracts» üblich ist. Z. B. stehen Dihydrofurane unter Furane, Dihydro-. Griechische Buchstaben und Einzelbuchstaben, die vom eigentlichen Namen durch Bindestrich getrennt sind, werden bei der alphabetischen Anordnung nicht berücksichtigt, z. B. stehen «O-Acetyl-derivate» unter A.

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  isoindoles
  isoquinolines
  julolidines
  phenanthridines (9-aza-phenanthrenes)
  pyridines
  pyridino[2,3-d]tropolones
  pyrroles
  quinolines
  quinolizidines
  spirocyclopropanopyrrolines
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  selenophenes
  9-thiafluorenes
  2-thianaphthalenes
  thianaphthenes (benzo-thiophenes)
  thiazanthenes
  thiophenes
  with 2 O-atoms
  benzo-1,4-dioxanes
  benzo-1,3-dioxoles
  chromono(2′,3′,3,4)coumarins
  chromono(3′,2′,3,4)coumarins
  m-dioxanes
  p-dioxanes
  1,3-dioxolanes
  α-pyrono(5′,6′,3,4)coumarins
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  cinnolines (1,2-diazanaphthalenes)
  dianthranilides
  1,3-diazacycloalkenes
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  pyrazoles
  pyridazines
  9(H)-pyrid[3,4-b]indoles
  pyrido[1,2-a]benzimidazoles
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  1,4-azaphosphorines
  benzisoxazoles
  benzo-1,4-thiazines
  benz-1,3-oxathioles
  benz-1,3-oxazines
  benz-3,1-oxazines
  benzoxazoles
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1,3-oxathioles
1,2-oxazines
1,3-oxazines
1,4-oxazines (morpholines)
oxazoles
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phenarsazines
phenoxathiins
phenoxazines
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thetins
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thiazoles
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benzofurazans
benzo-1,2,4-thiadiazines
benzothiadiazoles
1,2,4-benzotriazines
copazolines (2,4,6-triazanaphthalenes)
1,3,4-dioxazolines
imidazothiazoles
1,2,4-oxadiazoles
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pyrano(3′,4′:5,6)-1,3-dioxins
sydnones
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triazoles
trioxaadamantanes
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sulfinetriazines
purines
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Acylierung	Acylation
Aether	Ethers
Aethyl-	Ethyl-
Alkoholate	Alkoxides
Alkohole	Alcohols
Alkylidenacetessigester	Alkylideneacetoacetic esters
Alkylierung	Alkylation
Allylumlagerung	Allyl rearrangement
Ameisensäure	Formic acid
Amidosulfonsäure	Sulfamic acid
Anhydrozucker	Anhydrosugars
Anlagerung	Addition
Arylierung	Arylation
Asparaginsäuren	Aspartic acids
Aufbau	Synthesis
Austausch	Replacement
Benzolringsystem	Benzene ring system
Benzopersäure	Perbenzoic acid
Bernsteinsäure	Succinic acid
Bimsstein	Pumice
Blei	Lead
Bor	Boron
Borsäure	Boric acid
Borsäureanhydrid	Boron trioxide
Brenztraubensäure	Pyruvic acid
Brom	Bromine
Brom-	Bromo-
Bromcyan	Cyanogen bromide
Bromjod	Iodine bromide
Carbäthoxylierung	Carbethoxylation
Carbonsäure-	Carboxylic acid-
Carbonsäuren, verzweigte	Carboxylic acids, branched
Chlor	Chlorine
Chlor-	Chloro-
Chloressigsäure	Chloroacetic acid
Chlorjod	Iodine monochloride
Chlorschwefel	Sulfur monochloride
Chrom	Chromium
Chin-	Quin-
Cumarin	Coumarin

	siehe unter
Dehydratisierung	Dehydration
Dehydrierung	Dehydrogenation
Diazokupplung	Diazo coupling
Dithiocarbonsäuren	Carbodithioic acids
Einführung von funktionellen Gruppen	Replacement of hydrogen
Eisen	Iron
Erdalkalien	Earths, alkaline
Erden, seltene	Earths, rare
Fluorwasserstoffsäure	Hydrogen fluoride
Gallensäurederivate	Bile acid derivatives
Glycerine	Glycerols
Halbacetale	Hemiacetals
Halogenide	Halides
Halogenwasserstoff	Hydrogen halide
Harnsäuren	Uric acids
Harnstoff	Urea
Heterocyclen	Heterocyclics
Holzkohle	Charcoal
Hydrierung	Hydrogenation
Hypohalogenite	Hypohalites
Isocyclen	Isocyclics
Isothioharnstoffe	Isothioureas
Jod	Iodine
Jod-	Iodo-
Jodwasserstoffsäure	Hydrogen iodide
Kalium	Potassium
Kern	Nucleus
Kettenverlängerung	Chain lengthening
Kohlehydrate	Carbohydrates
Kohlendioxyd	Carbon dioxide
Kohlensäure	Carbonic acid
Kohlenwasserstoffe	Hydrocarbons
Kugelmühlenreaktor	Ball mill reactor
Kunstharz-Base	Resin base
Kupfer	Copper
Kupplung	Coupling
Mangan	Manganese
Molekülverbindungen	Molecular compounds
Natrium	Sodium
Natriumäthylat	Sodium ethoxide
Oxydation	Oxidation
Peressigsäure	Peracetic acid
Phenyljodidchlorid	Iodobenzene dichloride
Phosphinsäuren	Phosphonic acids
Polymerisierung	Polymerization

	siehe unter
Quecksilber	Mercury
Razemate	Racemates
Reduktions-Tropfverfahren	Dropping reduction
Rhodan	Thiocyanogen
Rhodanid	Thiocyanate
Ringerweiterung	Ring enlargement
Ringöffnung	Ring opening
Ringschluß	Ring closure
Ringverengung	Ring contraction
Salpetrigsäureester	Nitrous acid esters
Salpetersäure	Nitric acid
Schutz	Protection
Schwefel	Sulfur
Schwefelchloride	Sulfur chlorides
Schwefelwasserstoff	Hydrogen sulfide
Seitenketten	Side chains
Senföle	Isothiocyanates
Silicium	Silicon
Siliciumdioxyd	Silica
Spaltung	Cleavage
Stellungswechsel	Position shift
Stickoxydul	Nitrous oxide
Stickstoff	Nitrogen
Stickstoffwasserstoffsäure	Hydrazoic acid
Sulfaminsäuren	Sulfamic acids
Sulfopersäure	Peroxymonosulfuric acid
Thiohalogenide	Sulfenylhalides
Thioharnstoff	Thiourea
Thiokohlensäuredisulfide	Disulfurdicarbothionates
Tschitschibabin	Chichibabin
Tschugaeff	Chugaeff
Umacylierung	Transacylation
Umesterung	Transesterification
Umkehrung	Inversion
Umlagerung	Rearrangement
Unterphosphorigsäure	Hypophosphorous acid
Verbindungen	Compounds
Veresterung	Esterification
Verseifung	Hydrolysis
Wanderung	Migration
Wasserstoffperoxyd	Hydrogen peroxide
Wismutverbindungen	Bismuth compounds
Wolfram	Tungsten
Wolframsäure	Tungstic acid
Zinn	Tin
Zuckersäuren	Saccharic acids

Abbreviations - Abkürzungen

abs.	absolute	absolut
alc.	alcoholic	alkoholisch
aq.	aqueous	wäßrig
ar.	aromatic	aromatisch
atm.	atmosphere(s)	Atmosphäre(n)
cf.	compare	vergleiche
concd.	concentrated	konzentriert
d.	density	Dichte
dil.	diluted	verdünnt
et al.	and others	und andere
E.	example	Beispiel
e.g.	for example	zum Beispiel
F. e. s.	Further example(s) see	weitere(s) Beispiel(e) siehe
hr(s).	hour(s)	Stunde(n)
liq.	liquid	flüssig
min.	minutes	Minuten
N	normal	normal
prepn.	preparation	Darstellung
prim.	primary	primär
s.	see	siehe
s. a.	see also	siehe auch
satd.	saturated	gesättigt
sec.	secondary	sekundär
soln.	solution	Lösung
startg. m. f.	starting material for (the preparation of...)	Ausgangsmaterial für die Darstellung von...
subst.	substituted	substituiert
sym.	symmetrical	symmetrisch
temp.	temperature(s)	Temperatur(en)
tert.	tertiary	tertiär
v.i.	via intermediates	über Zwischenprodukte
w.a.r.	without additional reagents	ohne Hilfsstoffe
Y *)	yield	Ausbeute

*) When yields are listed in parentheses, the yields so designated refer to the immediately preceding step of a multi-step reaction.

Bei mehrstufigen Synthesen beziehen sich eingeklammerte Ausbeuteangaben auf die unmittelbar vorhergehende Stufe.

Symbols - *Zeichen*

(on the right half of the page)		(auf der rechten Hälfte der Seite)
Electrolysis	↯	Elektrolyse
Ring closure	○	Ringschluß
Ring opening	↻	Ringöffnung
'see title on the left half of the page'	←	«siehe Titel auf der linken Hälfte der Seite»

Journal Abbreviations - *Zeitschriften-Abkürzungen*

A.	Liebig's Annalen der Chemie
A. ch.	Annales de Chimie
Am. Soc.	Journal of the American Chemical Society
Ar.	Archiv der Pharmazie und Berichte der Deutschen Pharmazeutischen Gesellschaft
Ark. Kemi	Arkiv för Kemi, Mineralogi och Geologi
B.	Chemische Berichte
Biochem.Prep.	Biochemical Preparations
Bl.	Bulletin de la Société Chimique de France
C. A.	Chemical Abstracts
C. r.	Comptes rendus (Paris)
G.	Gazzetta Chimica Italiana
H.	Hoppe Seyler's Zeitschrift für physiologische Chemie
Helv.	Helvetica Chimica Acta
J. Org. Chem.	Journal of Organic Chemistry
J. pr.	Journal für praktische Chemie
M.	Monatshefte für Chemie
Org. Synth.	Organic Syntheses
R.	Recueil des Travaux Chimiques des Pays-Bas
Ж	Journal of General Chemistry (Russia)
Soc.	Journal of the Chemical Society
Synth. Meth.	Synthetic Methods of Organic Chemistry

For other journal abbreviations see Beilstein, Handbuch der organischen Chemie or Chemical Abstracts.

Die übrigen Zeitschriften-Abkürzungen siehe Beilsteins Handbuch der organischen Chemie oder Chemical Abstracts

Systematic Survey - *Systematische Uebersicht*

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Reagents - Hilfsstoffe

Volumes 1–10 Band 1–10

w.a.r.(heat,irradiation,↯, electric discharge, ultrasonic waves)
Li, Na, Na/K, K
LiH, NaH
Na,Hg
Na_2O
Bases
Alkalies
Alkali hydroxide
Aq. alkali hydroxide
LiOH, NaOH, KOH
Alkali in water a. alcohol
NaOH/alcohols
KOH/alcohols
Na/alcohol, NaOR, (Sodium compound)
$NaOCH_3$, $NaOC_2H_5$, $NaOC_4H_9$-n
K/alcohol, KOR
K-isopropoxide, K-tert-butoxide
n-C_4H_9Li, C_6H_5Li
$(C_6H_5)_3C\cdot Na$
Alkali amide
Li/liq. NH_3, Li/liq. NH_3/alcohol, $LiNH_2$, $(C_2H_5)_2NLi$, Li-methylanilide
Na/liq. NH_3, $NaNH_2$, Na-anilide
K/liq.NH_3, KNH_2
Alkali in pyridine
Na_2O_2
Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$
HCOONa
CH_3COONa, CH_3COOK
Na-citrate
Alkali cyanide, NaCN, KCN
KOCN
NaSCN, KSCN
NaN_3
$NaNO_2$, KNO_2
$NaNO_3$, KNO_3
KH_2PO_4
K-xanthate
Na_2S, Na_2S_2, Na_2S_x, NaHS
Na_2Se_x
KHS
$Na_2S_2O_3$
Na_2SO_3, K_2SO_3, $Na_2S_2O_5$ (pyrosulfite), $NaHSO_3$
Na_2SO_4
NaF, KF, KHF_2
LiCl
Alkali iodides, NaI, KI
Alkali salts
Alkaloid-alkali salts
Na^+, K^+
NH_3
Organic bases
Resin base
Triton B, Choline, BTAB
Amines
Amines, prim., Alkylamines
Methyl-, n-Butyl-, Benzylamine
Dimethylamine, Diethylamine, Dicyclohexylamine, Morpholine
Tert. amines, Trialkylamines, Trimethylamine, Triethylamine
Piperidine, N-Ethylpiperidine, N-Methylmorpholine
Aniline
Dialkyl-, Dimethyl-, Diethylaniline
Pyridine, Lutidine, Collidine, Quinoline
Cu, Ag, Ag-Cu, Cu,Mg
Copper oxide, Cu_2O, CuO
$Cu(OH)_2$
AgOH
Copper borate
$Cu\cdot C\equiv C\cdot C_6H_5$
Ag_2CO_3
CH_3COOAg, CF_3COOAg
$CuCO_3$, Cupric carbonate, basic
$(CH_3COO)_2Cu$
Fehling solution
CuCN
CuSCN
Cu(I,II) sulfite
CuHal, CuCl, CuBr/Mg, CuI/Mg, $CuCl_2$
Cu^+, Cu^{++}
C_6H_5COOAg
AgCN
AgN_3
$AgNO_2$
$AgNO_3$
AgF-Cu
Ag^+
CaH_2
CaO, BaO, BaO-SiO_2
$Ca(OH)_2$, $Ba(OH)_2$
$Ba(OR)_2$
CaC_2, Ca/NH_3
$(CH_3COO)_2Ba$
$CaCO_3$, $BaCO_3$
$CaSO_4$
$CaCl_2$, $BaCl_2$-C
Mg, Mg,Hg, Mg/MgI_2
Zn, Zn,Cu, Zn,Hg
Cd, Hg
MgO, ZnO, HgO
$Mg(OH)_2$
$Mg(OR)_2$
RMgHal, CH_3MgI, C_6H_5MgBr
R_2NMgBr, $C_6H_5N(CH_3)$-MgBr
Zinc alkyls, Zinc alkyl halides
Organomercury compounds
$CdCO_3$
Mercury resin

$(CH_3COO)_2Hg$
$Zn(CN)_2$, $Hg(CN)_2$
$Hg(ONC)_2$ (fulminate)
$Mg(NO_3)_2$
$BeSO_4$, $MgSO_4$, $HgSO_4$
$MgCl_2$, $MgBr_2$
$ZnCl_2$, $ZnCl_2 \cdot 2NH_3$
$CdCl_2$
$HgCl/CdCO_3$
$HgHal_2$, $HgCl_2$, $HgBr_2$, HgI_2
Mg^{++}, Ca^{++}, Zn^{++}, Hg^{++}
Al, Al,Cu, Al,Hg
$NaBH_4$, $LiBH_4$
$LiAlH_4$
$NaBH(OCH_3)_3$
$Na_2B_4O_7$
B_2O_3, HBO_2
$B(OR)_3$
Sodium perborate
Al_2O_3
TiOH
TlOR
$Al(OR)_3$
Al-isopropoxide, Al-tert-butoxide, Al-phenoxide
Al silicate
Clay, Superfiltrol
Pumice
Glass powder
$AlPO_4$/water glass
BF_3
HBF_4
$Al(Hal)_3$, $AlCl_3$, $AlBr_3$
Al^{+++}
Ce and rare earths
C
p-Cymene
Cyclohexene
CH_3OH, C_2H_5OH
Trimethylene glycol
Glycerol
$HOCH_2CH_2OCH_3$-(Methyl Cellosolve)
Methoxyacetylene
Ethylene oxide
Glucose
Hydroquinone
Oxo compounds
Formaldehyde, Benzaldehyde, Acetone
Benzophenone

Quinones
Dichlorodicyanoquinone
Ketene
D-Lactose hydrate
Pyruvic acid
Acetals
$(NH_4)_2CO_3$
$HCOONH_4$, CH_3COONH_4
NH_4SCN
Salts of organic bases
Carbonates of org. bases
Acetates of organic bases
Diethylamine acetate
Tetramethylammonium acetate
Piperidinium acetate
Diazomethane
Hexamethylenetetramine
$HCONH_2$, CH_3CONH_2
$HCON(CH_3)_2$
$CO(NH_2)_2$
Phenyl isocyanate
Carbodiimides
N,N′-Dicyclohexylcarbodiimide
2,4-Diguanidinophenyl lauryl ether
Fungi (Mold), Yeast
Aspergillus oryzae enzyme, Chymotrypsin, Emulsin, Hog kidney enzyme, Isomerase, Papain, Pseudomonas extract
Acetobacter suboxydans, Streptococcus faecalis
Cyanohydrins
Nitrosobenzene
Nitrosodimethylaniline
Isonitrosocyanoacetic esters
Isopropane nitronate
2-Nitropropane
Nitro compounds, ar.
Nitrobenzene
Carboxylic acid esters
Ethyl malonate
$(CH_3CO)_2O$, $(C_2H_5CO)_2O$, $(CF_3CO)_2O$
Peroxides
Ascaridole
Acyl peroxides

Acetyl-, Benzoyl peroxide
Ion exchange resin, Anion - -, Cation - -
Amberlite, Duolite
Dowex-50, Dowex-50-H^+
Phenol, Resorcinol, Pyrogallol
Aminoacids
Buffer pH 4.6-4.8
$HCOOH$, CH_3COOH, CH_3CH_2COOH
Tartaric acid
Salicylic acid
H_2NCH_2COOH
Thioacetic acid
$ClCH_2COOH$, CCl_3COOH
$(COOH)_2$, $CH_2(COOH)_2$, Phthalic acid
CO_3^{--}, CO_3H^-
Peroxy acids
$HCOO_2H$, CH_3COO_2H
CF_3COO_2H
$C_6H_5COO_2H$, Perphthalic acid
RSH, Arylmercaptans
Thiourea
Thioureas
Thiocyanates
Dimethyl sulfate
Sulfonamides
Amyl disulfide
Methyl tetrasulfide
C_6H_5IO
$C_6H_5I(OAc)_2$ (phenyl iodosoacetate)
Alkyl iodide, CH_3I, C_2H_5I
Allyl bromide
Polyhalogenoalkanes
CCl_3H, CCl_3Br
Benzotrichloride
o-Chlorotoluene
Iodobenzene dichloride
BrCN, ICN
N-Chlorodiethylamine
N-Halogenamides
Bromoacetamide
Chlorourea
N-Halogenimides
N-Halogenosuccinimide
N-Chloro-, N-Bromo, N-Iodosuccinimide
Bromophthalimide

Chloramin-T
Chloranil
$COCl_2$
$RCOCl$, CH_3COCl
$(COCl)_2$
C_6H_5COCl, C_6H_5COBr
$(CH_3)_2CHCHBrCOBr$
SiO_2, SiO_2-Al_2O_3
$TiO_2/HCOOH$
$SiCl_4$, $TiCl_4$
Sn
$SnCl_2$, $SnCl_4$
PbR_4
PbO, Pb_3O_4, PbO_2
$Pb(OH)_2$
$Pb(OH)_2\cdot PbCO_3$, $PbCO_3$
$(CH_3COO)_2Pb$
$(CH_3COO)_4Pb$
$Pb(NO_3)_2$
Pb^{++}
ThO_2
Dicyanodiamide
Phenylhydrazine
$H_2N\cdot NH_2$, $C_6H_5NHNH_2$
N_3^-, HN_3
NH_2OH
Nitrogen oxides
N_2O, NO (nitric oxide), N_2O_3, N_2O_4, N_2O_5
NH_4NO_3
Alkyl-, Butyl-, Amyl nitrite
NO_2^-
NOCl, NOBr
Alkyl nitrate
Acetyl nitrale
Nitrates
HNO_3
P
Phosphorus compounds
PH_4I
$(C_6H_5)_3P$
Phosphazo compounds
Trichlorophosphazosulfonyl compounds
P_2O_5
$(C_6H_5O)_3P$
Tetraethyl pyrophosphite
$H_2PO_2^-$
H_3PO_2
Quinoline phosphate
Dialkyl chlorophosphate
Phosphat butter
$(HPO_3)_3$
$H(PO_3H)_xOH$
H_3PO_4
P_2S_3, P_4S_7, P_2S_5
Triphenyl phosphite methiodide
P_2I_4
$PHal_3$, PCl_3, PBr_3
Phenylphosphoryl dichloride
$POCl_3$, $POBr_3$
$PSCl_3$
$PHal_5$, PCl_5
As_2O_3, As_2O_5
$AsCl_3$
SbF_3, $SbCl_3$, $SbCl_5$
Bi
Bi_2O_3
BiO_3^-
Bismuth carbonate
NH_4-vanadate
V_2O_5
V_2O_5,Al_2O_3
O_2, O_3
H_2O_2
Peroxide
S
S^{--}, S_2^{--}, S_x^{--}
$(NH_4)_2S$, $(NH_4)_2S_x$
SH^-, SH_2
Na-formaldehyde-sulfoxylate
$S_2O_4^{--}$
Tetrathionate
$SO(NH_2)_2$
RSO_2NH_2
$SOCl_2$, $SOBr_2$
RSO_2Cl
Arylsulfonyl chloride
Benzene-, p-Toluene-, p-Acetylaminobenzenesulfonyl chloride
SO_2Cl_2
SO_2
$S_2O_5^{--}$
SO_3
$(NH_4)_2SO_3$
$(NH_4)_2SO_4$
Sulfates of org. bases
Pyridine·SO_3, Dioxane·SO_3
$HCON(CH_3)_2\cdot SO_3$
$NaHSO_4$, $KHSO_4$, NH_4HSO_4
Sulfonates
$C_6H_5SO_3NH_4$
Alkanesulfonic acids, Ethanesulfonic acid
Benzene-, p-Toluene-, m-Xylene-,Napthalen β-sulfonic acid
Na-m-nitrobenzenesulfonate
$HOOC\cdot CH_2\cdot SO_2H$ (sulfacetic acid)
Sulfosalicylic acid
Sulfanilic acid
$HOCH_2SO_4Na$ (hydroxy methylenesulfonate)
$H_2NSO_3^-$, H_2NSO_3H
NH_2OSO_3H (hydroxylamine-O-sulfonic acid
$ONOSO_3H$ (nitrosyl sulfate)
$ON(SO_3K)_2$ (nitrosodisulfonate)
H_2SO_4
H_2SO_5
S_2O_3
$(NH_4)_2S_2O_8$
$S_2O_8^{--}$
FSO_3H, $ClSO_3H$
Sulfur chlorides, S_2Cl_2, SCl_2
Se
SeO_2
Cr-Cu-C
Chromite
$CuCr_2O_4$, $CuCr_2O_4$-C
$(Ca,Cu)Cr_2O_4$, $(Ba,Cu)Cr_2O_4$
Cr_2O_3,Al_2O_3
MoO_x, MoO_3
MoO_3-Al_2O_3, MoO_3-SiO_2
CrO_4^{--}, $Cr_2O_7^{--}$, CrO_3, CrO_3-C_5H_5N
t-Butyl chromate
$CrCl_2$
CrO_2Cl_2
MoS_2, WS_2
$(IO)_2SO_4$ (iodyl sulfate)
I_3^-
Halogen, Cl, Br, I

$BrCN$, ICN
IF_5, ICl, ICl_3, IBr
Alkyl hypochlorite, tert-C_4H_9OCl
$CF_3COOHal$
$HalO^-$, ClO^-
$NaOCl$, $KOBr$, KOI, $Ca(OCl)_2$, $Ba(OI)_2$
$HOCl$
ClO_3^-, BrO_3^-
$KClO_3$, $NaBrO_3$, KIO_3
HIO_3
$HClO_4$, $AgClO_4$
IO_4^-, HIO_4
Cl^-, I^-
NH_4F, NH_4Cl, NH_4I
Hydrochlorides, Hydrobromides, Hydriodides
Trimethylamine hydrochloride, Pyridine-, Quinoline-
Acetylpyridinium chloride
Methiodides
Tetraethylammonium bromide
Pyridinium ethiodide
$(CH_3)_4NBr \cdot Br_2$
$C_5H_5N \cdot Br_2$
Pyridine hydrobromide-perbromide
Triphenyl phosphite methiodide
Acids/metal chlorides
Mineral acids
Hydrogen halides, HF, HCl, HBr, HI
$MnCO_3$
$(CH_3COO)_2Mn$
MnO_2
K_2MnO_4
MnO_4^-
$NaMnO_4$, $KMnO_4$, $Ba(MnO_4)_2$
Fe
Fe/Fe^{++}
FeS/Al_2O_3
$FeSO_4$
$Fe_2(SO_4)_3$
$FeCl_2$, $FeCl_3$
Fe^{+++}
$Na_3[Fe(CN)_5NH_3]$
$K_3[Fe(CN)_6]$
Co
Co/Al_2O_3
Cr_2O_3*-cobalt hydrate-*$CaCO_3$
Cu-Co-Cr-asbestos
$Co(CO)_4$
$(CH_3COO)_2Co$
Co nitrite
Co-polysulfide
$CoCl_2$
CoF_3
Ni
Ni-Al
Ni/Pt, $Ni/PtCl_4$
Ni, Cr_2O_3
Nickel-zinc chromite
$Ni(CO)_4$
Ni-acetylacetonate
$NiSO_4$
Ru-C
RuO_2, RuO_4
Pd
Pd-$CaCO_3$, *Pd-*$SrCO_3$, *Pd-*$BaCO_3$
Pd-$BaSO_4$
Pd-C
Pd-pumice
PdO
$PdCl_2$*-C*
OsO_4
Pt
Pt-C
PtO_2
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